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School of Graduate Studies

(Department of Chemical and Petroleum Engineering)

This is to certify that the undersigned have read and recommended to the Committee on Graduate Studies for acceptance, a thesis submitted by Jack Eng, B.A.Sc. in Chemical Engineering, entitled:

THE CATALYTIC OXIDATION

OF

REDWATER ASPHALT BASE STOCK

(The Air Blowing of Vacuum Reduced Redwater Asphalt Base Stock with Special Reference to use of Phosphorus Pentoxide as a Catalyst)

Professor _____

Professor _____

Professor _____

THE CATALYTIC OXIDATION OF REDWATER ASPHALT BASE STOCK

The Air Blowing of Vacuum Reduced Redwater Asphalt Base Stock with Special Reference to use of Phosphorus Pentoxide as a Catalyst

Submitted in Partial Fulfillment
of the
Requirements for the Degree of
Master of Science
in Chemical Engineering

by

Jack Eng

Under the direction of

Dr. G. W. Govier
and
Dr. D. Quon

University of Alberta,
Department of Chemical and Petroleum Engineering,
Edmonton, Alberta.

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The Research Problem

The investigation undertaken was an experimental study of the air blowing of vacuum reduced Redwater asphalt base stock with special reference to the use of phosphorus pentoxide as an addition agent. The specific objectives of the problem were:

(1) To determine the changes in the properties of the asphalt base stock as it is air blown under various blowing temperatures and various air rates without phosphorus pentoxide.

(2) To determine the changes in the properties of the asphalt base stock as it is air blown under various blowing temperatures and various air rates with phosphorus pentoxide.

(3) To compare the results obtained with phosphorus pentoxide with those obtained without phosphorus pentoxide.

SUMMARY

Redwater asphalt base stock was air blown in a conventional vertical cylindrical still approximately 10 inches in diameter and 30 inches in height. The base stock was initially blown without the use of phosphorus pentoxide at temperatures of 465 °F. and 525 °F., and air rates of 55 and 75 cubic feet per minute per ton of charge. In the next series of experiments the base stock was blown with the use of phosphorus pentoxide as a "catalyst". Three tests were made at a fixed air rate of 55 cubic feet per minute per ton of charge and at a blowing temperature of 525 °F. with 0.25, 0.50 and 1.0 percent phosphorus pentoxide respectively. As with the straight air blown tests the effect of varying the operating conditions was investigated. At the end of a phosphorus pentoxide test, considerable residue was present in the bottom of the still. The effect of re-using the residue formed from a 0.50 percent pentoxide test was studied. Different methods of dispersing the phosphorus pentoxide were employed. With the operating conditions fixed at a blowing temperature of 525 °F. and at an air rate of 55 cubic feet per minute per ton of charge, 1.0 percent phosphorus pentoxide was dispersed into the asphalt by grinding in a mortar and pestle, by hand stirring, by use of carbon tetrachloride and finally by the use of a 100 mesh screen $2\frac{3}{4}$ inches from the still bottom in addition to grinding in a mortar and pestle.

It was found that by air blowing the Redwater asphalt

base stock, a very wide range of closely controlled products could be obtained. The chemical and physical changes which the base stock undergoes were not well understood but the product was harder (lower penetration), heavier, lower in ductility, and higher in softening point than before the blowing. The fractional composition was also found to change with air blowing, the resins decreasing and the asphaltenes increasing. The oily constituents changed comparatively little. Furthermore, the mean molecular weights of the asphaltenes, resins and oily constituents were increased markedly by air blowing.

The use of small amounts of phosphorus pentoxide as a "catalyst" showed to a great advantage in controlling the hardness of the blown asphalts. At a given softening point a pentoxide blown product could be prepared which had a higher penetration than a straight blown asphalt. Under similar blowing conditions and with the same dispersion method, the penetration increase was dependent on the amount of pentoxide used, at least within the range of zero to one percent. The method of dispersing the phosphorus pentoxide was found to be comparable in importance to the amount of pentoxide used. With a better dispersion method, a greater increase in penetration (as referred to a given softening point) was obtained. It was also found that the same type of effect may be accomplished by the re-use of the residue formed from a pentoxide test.

In both the straight and "catalytic" air blowing the effect of different blowing temperatures and different air rates, while important as far as reaction rate is concerned, was very slight on the relationships between the properties of the blown asphalt and its softening point.

Acknowledgment

The author wishes to take this opportunity to extend sincere thanks to all those who have assisted in this investigation:

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TABLE OF CONTENTS

The Research Problem

Summary

Acknowledgment

List of Tables

List of Figures

Page

I. Introduction 1

II. Literature Review 3

III. Industrial Practice 9

IV. Experimental Program 12

V. Equipment 13

VI. Experimental Procedures 19

VII. Experimental Results 24

VIII. Discussion of Results 39

Series 1 - Straight Air Blowing 39
Effect of Temperature and Air Rate on Reaction Time 39
Effect of Temperature and Air Rate on Penetration, Viscosity, Ductility, Softening Point Relationships 40

Series 2 - Air Blowing with Phosphorus Pentoxide "Catalyst" 40
Effect of Phosphorus Pentoxide on Reaction Time 40
Effect of Temperature and Air Rate 41
Effect of Phosphorus Pentoxide on Penetration, Viscosity, Ductility, Softening Point Relationships 42
Effect of Pentoxide Residue 44
Effect of Phosphorus Pentoxide on Asphaltenes, Resins and Oily Constituents 47

Page

Series 3 - Air Blowing with Phosphorus Pentoxide Dispersed by Different Methods 51
Effect of Dispersion Method on Reaction Time 51
Effect of Dispersion Method on Penetration, Viscosity, Ductility, Softening Point Relationships 54
Effect of Straight and "Catalytic" Air Blowing on Specific Gravity and Solubility in Carbon tetrachloride 55

IX. Conclusions 84

APPENDICES

I. Analysis of the Residue 86

II. Test Methods 87

III. Determination of Asphaltenes, Resins and Oily Constituents 88

IV. Procedure for Determining Molecular Weights of Asphaltenes, Resins and Oily Constituents 89

Bibliography 91

LIST OF TABLES

Page

I. Properties of Vacuum Reduced Redwater Asphalt Base Stock 26

II. Air Blowing, 0 percent Phosphorus Pentoxide, 465 °F., 55 cubic feet per minute per ton of charge 27

III. Air Blowing, 0 percent Phosphorus Pentoxide, 525 °F., 55 cubic feet per minute per ton of charge 28

IV. Air Blowing, 0 percent Phosphorus Pentoxide, 525 °F., 75 cubic feet per minute per ton of charge 29

V. Air Blowing, 0.25 percent Phosphorus Pentoxide, Mortar and Pestle, 525 °F., 55 cubic feet per minute per ton of charge 30

VI. Air Blowing, 0.50 percent Phosphorus Pentoxide, Mortar and Pestle, 525 °F., 55 cubic feet per minute per ton of charge 31

VII. Air Blowing, 1.0 percent Phosphorus Pentoxide, Mortar and Pestle, 525 °F., 55 cubic feet per minute per ton of charge 32

VIII. Air Blowing, 0.50 percent Phosphorus Pentoxide, Mortar and Pestle, 465 °F., 55 cubic feet per minute per ton of charge 33

IX. Air Blowing, 0.50 percent Phosphorus Pentoxide, Mortar and Pestle, 525 °F., 75 cubic feet per minute per ton of charge 34

X. Air Blowing, Residue, 0.19 percent Phosphorus Pentoxide, Mortar and Pestle, 525 °F., 55 cubic feet per minute per ton of charge 35

XI. Air Blowing, 1.0 percent Phosphorus Pentoxide, Hand Stirring, 525 °F., 55 cubic feet per minute per ton of charge 36

XII. Air Blowing, 1.0 percent Phosphorus Pentoxide, Carbon Tetrachloride, 525 °F., 55 cubic feet per minute per ton of charge 37

XIII. Air Blowing, 1.0 percent Phosphorus Pentoxide, Mortar and Pestle and Screen, 525 °F., 55 cubic feet per minute per ton of charge 38

LIST OF FIGURES

		Page
1.	Pilot Still - Dimensional Drawing	15
2.	Pilot Still - Photograph	16
3.	Spiral Air Coil	17
4.	Spiral Air Coil in Still	18
5.	Effect of Blowing Temperature and Air Rate on Reaction Time	57
6.	Effect of Blowing Temperature on Penetration at 32 °F., 200 gm, 60 sec	58
7.	Effect of Blowing Temperature and Air Rate on Penetration at 77 °F., 100 gm, 5 sec	59
8.	Effect of Blowing Temperature on Penetration at 100 °F., 100 gm, 5 sec	60
9.	Effect of Blowing Temperature on Penetration at 115 °F., 50 gm, 5 sec	61
10.	Effect of Blowing Temperature on Saybolt Furol Viscosity	62
11.	Effect of Blowing Temperature on Ductility	63
12.	Effect of Phosphorus Pentoxide on Reaction Time	64
13.	Effect of Blowing Temperature and Air Rate on Reaction Time	65
14.	Effect of Blowing Temperature and Air Rate on Penetration at 77 °F., 100 gm, 5 sec	66
15.	Effect of Phosphorus Pentoxide on Penetration at 32 °F.	67
16.	Effect of Phosphorus Pentoxide on Penetration at 77 °F.	68
17.	Effect of Phosphorus Pentoxide on Penetration at 100 °F.	69
18.	Effect of Phosphorus Pentoxide on Penetration at 115 °F.	70
19.	Effect of Phosphorus Pentoxide on Saybolt Furol Viscosity	71
20.	Effect of Phosphorus Pentoxide on Ductility	72

Page

21. Effect of Phosphorus Pentoxide on the Fractional Composition 73

22. Effect of Phosphorus Pentoxide on the Mean Molecular Weight of Asphaltenes, Resins and Oily Constituents 74

23. Effect of Dispersion Method for Phosphorus Pentoxide on Reaction Time 75

24. Effect of Dispersion Method for Phosphorus Pentoxide on Penetration at 32 °F., 200 gm, 60 sec 76

25. Effect of Dispersion Method for Phosphorus Pentoxide on Penetration at 77 °F., 100 gm, 5 sec 77

26. Effect of Dispersion Method for Phosphorus Pentoxide on Penetration at 100 °F., 100 gm, 5 sec 78

27. Effect of Dispersion Method for Phosphorus Pentoxide on Penetration at 115 °F., 50 gm, 5 sec 79

28. Effect of Dispersion Method for Phosphorus Pentoxide on Saybolt Furol Viscosity 80

29. Effect of Dispersion Method for Phosphorus Pentoxide on Ductility 81

30. Effect of Air Blowing on Specific Gravity 82

31. Effect of Phosphorus Pentoxide on Solubility in Carbon Tetrachloride

I. INTRODUCTION

Asphalt has been known to man for some five or six thousand years. In the early periods, the asphalt used was native asphalt, formed by the natural distillation of oil. Today, although there are still large deposits of native asphalt, most of the asphalt is manufactured from crude oil refining.

There are at present many uses of asphalt. It is used as paving material for highways and runways of airports, in roofing and waterproofing material, pipe linings and coatings, paints and varnishes, crack-filling materials, and for numerous other purposes.

Because of the variety of uses of asphalt, it is necessary to prepare products which differ widely in certain important physical properties. One of the most important processes for preparing such products is by blowing air at elevated temperatures through residual oils. These air blown asphalts appear to acquire a certain amount of pliability, elasticity and resilience. They are less ductile at ordinary temperatures than residual asphalts of the same penetration, but are less susceptible to temperature changes and are consequently favored where wide temperature ranges have to be met. For equal softening points the penetration of blown asphalts is greater than that of residual asphalt.

The degree of blowing depends upon the choice of feedstock, and the extent of the "blown" characteristics of the

asphalt can be controlled but only within certain limits. It was reported (14) that the use of small amounts of phosphorus pentoxide as a "catalyst" would permit a further alteration of the "blown" characteristics. At a given softening point a "catalytic" product can be prepared which has a higher penetration than a straight blown asphalt; or at a given penetration the softening point can be increased. Thus residua which by ordinary air blowing yield products which fail to meet penetration specifications can successfully be manufactured with the aid of "catalysts". Instead of blowing light residua to obtain products low in temperature susceptibility, heavier residua with higher flash point can be air blown with help of "catalysts" to the same softening point and penetration relationship.

Asphalt from Redwater crude was selected as the most suitable asphaltic material to study for two reasons. First, high softening point grades of roofing asphalts cannot be manufactured from Redwater crude residua by straight air blowing because of failure to meet penetration specifications. Secondly, Redwater is one of the Alberta's most prolific producers of mixed base crude generally suitable for asphalt production.

II. LITERATURE REVIEW

In 1865 Gesner (12) reported that the properties of petroleum products changed when treated with oxidizing agents or air. However, it was Francis X. Byerley (6) who in 1894 first manufactured blown asphalt on a commercial scale. He heated petroleum residuum in a closed shell still to about 600 °F. and passed a small quantity of air through it. With this small amount of air this process was essentially a distillation process, with the air used principally for agitation and to accelerate the distillation. G. K. Culmer (9) later described a process by which a large amount of air was forced through petroleum residuum at low temperatures. Comparatively small stills were used and the air was introduced into the heated residuum by a single perforated pipe laid along the bottom of the still. Because of the quality, character, and light gravity of the residuum used in these early experiments, and because of the poor distribution of air through the heated residuum, the time of blowing varied from 20 to 60 hours. The Culmer process was without doubt the forerunner of the present methods used in air blowing residua and asphalt products of various types.

The use of addition agents to augment the air blowing process dates back to Jenny (19) in 1876. He patented the process of treating sludge oil with various compounds such as potassium permanganate, oxides of lead and manganese which

release oxygen and accelerate the air blowing process. Salathé (37) in 1896 described the use of various oxides or peroxides to accelerate the air blowing of asphalts to obtain a product with improved penetrating properties as a saturant for wood. Amongst other earlier investigators were De Smedt (10), Baillard (4), Busse (5), and Schreiber (38). A comprehensive general historical survey is given by Abraham (1).

It was not until 1930 that Abson (2) pointed out that use of salts such as ferric chloride and zinc chloride in addition to accelerating the blowing process produced asphalts of low brittleness at low temperatures and more resistant to flow at high temperatures. Abson was followed by a number of patentees who found various advantages in use of different agents or catalysts. Amongst these patentees, the most important is Hoiberg (14). He found that blown asphalt prepared by air blowing Smackover crude residua in the presence of red phosphorus or phosphorus containing catalyst such as P_2O_5, P_4S_3, P_4S_7, and P_2S_5 had a much higher penetration for a given softening point than if the crude were blown without "catalyst". The manufactured product was found suitable for protective coatings and roofing.

Although blown asphalts are often referred to as oxidized asphalts, the essential process, as postulated by Morris Katz of the National Research Council of Canada, is (21) not oxidation but condensation followed by polymerization to

form products of higher molecular weight. It is believed that the small amount of hydrogen removed combines with the oxygen to form water. Ultimate analyses of the blown asphalts showed no appreciable fixation of oxygen. The oxygen probably acts as a catalyst. It is believed (8) that the sulphur also plays an important part in promoting the reactions.

Asphalts have been separated by solvent extraction into different fractions. Le Bel (22) extracted bitumen with naphtha and then precipitated asphaltenes with amyl alcohol. Richardson (35) distinguished four components in asphalt - petrolenes, maltenes, asphaltenes and carbenes. Marcusson (25) modified the procedure extensively and his method is still widely used. He distinguished oily constituents, resins, asphaltenes, and asphaltic acids and their anhydrides in natural asphalts. Since acid constituents are either absent or present only in very small quantities in asphalts manufactured from petroleum products, most investigators usually speak only of asphaltenes, resins and oily constituents. Other components which are sometimes determined are carbenes and carboids. Other methods for determining the components of the asphalt are described by Strieter (39), Hoiberg and Garris (16), Hubbard and Stanfield (18), Cattel, Shea et al (7). They are all, however, based on Marcusson's procedure. It is important to remember that although the division of the constituents is used to a great extent, any slight variation in methods and reagents will give

different results. Also, the nature of asphaltenes, resins and oily constituents in different asphalts vary considerably.

Marcusson and Picard (26) found that the fractional composition changes with air blowing, the resins decreasing and the asphaltenes increasing. The oily constituents changed comparatively little. These same trends were also established by Morris Katz and later by Hoiberg (21, 13). Sachanen (36) stated that the oily constituents may be oxidized to resins, which in turn may be oxidized to asphaltenes. The properties of oily constituents, resins, and asphaltenes are discussed thoroughly by Mack (23), Murphy (27), Nellensteyn (28, 29, 30), Swanson (40), Sachanen (36), Pfeiffer and Saal (33). Morris Katz (21) maintained that in addition to variation in the fractional composition on air blowing, the mean molecular weight of the fractions increased markedly.

Such large changes in fractional composition are accompanied by changes in colloidal nature. Nellensteyn (28) postulated that asphaltenes consisted of a carbon nucleus surrounded by protective bodies. Thus the asphaltic bitumen consisted of carbon surrounded by layers of hydrocarbons in which the ratio of carbon to hydrogen become progressively lower; the outermost layer of this disperse phase having a ratio the same as that of the oily medium. Mack (23) agreed with Nellensteyn that asphalts constitute a lyophilic sol and that the asphaltenes formed the dispersed phase and resins and oily constituents

formed the dispersion medium; but he disagreed with Nellensteyn's contention that asphaltenes were composed of free carbon plus protective bodies. Pfeiffer and Van Doormaal (33) stated, on the strength of ultra microscopic examination, that it was scarcely likely that the nucleus of the dispersed phase should consist of elementary carbon. More recently, Preckshot (34) and D. L. Katz (20) examined asphalt in thin films under the electron microscope and concluded that the asphaltene particles, if present, are less than 65 Angstroms in diameter. This further indicated that asphaltenes could not be composed of free carbon. Eilers (11) has described very recently the relationship of the colloidal structure to flow properties of asphalts. He classified asphalts into three types: Newtonian, sol and gel.

Although "catalytic asphalt" is the term generally used to describe air blown asphalts obtained with the use of addition agents, the reaction is not strictly a catalytic one. The reaction rate may or may not be increased with the use of addition agents and in some cases it may even be decreased. In many reactions the addition agent is effective by forming complexes or intermediate products and hence cannot be recovered at the end of the reaction.

Practically nothing is known about why certain addition agents produce a product with higher penetration for a given softening point. Hoiberg (15) analyzed Arkansas asphalts

blown with and without phosphorus pentoxide. Although the pentoxide blown asphalt showed a very much higher penetration for a given softening point than the straight blown asphalt, the fractional composition of the two asphalts appear to be almost identical. Hoiberg states that perhaps the increased penetrations are due to the formation of asphaltene molecules of higher molecular weight than produced by straight air blowing. Such fractions could be expected to be less susceptible to peptization by the resin fractions. Evidently any changes brought about by addition agents are primarily the result of changes in the colloidal nature of the asphalt. Chemical reaction may also be a factor.

III. INDUSTRIAL PRACTICE

Blown asphalts are manufactured either by a batch or continuous process. In the batch process, two general types of stills are used, the horizontal and the vertical. The horizontal type is simply a large cylindrical vessel horizontally mounted, usually holding about 5000 gallons of charge. Heat is applied by direct fire and air is supplied by high capacity blowers. The vertical stills are cylindrical towers set upright having a capacity of from 6000 to 20000 gallons. Air is admitted through perforated pipes at the bottom of the still. Because the air is in contact with the charge for a longer period of time, vertical stills are more efficient. However, vertical stills require more complicated heating systems and a higher pressure air supply is needed due to the greater depth of asphalt.

In batch air blowing the still is charged with a base stock at approximately 450 ^{o}F. and the charge is then blown for a period of five to fifteen hours at an air rate of 30 to 75 cubic feet per minute per ton of asphalt. The air may be blown either through the still under pressure, or else drawn through the still by subjecting the contents of the still to partial vacuum up to 20 inches of mercury. The loss depends entirely upon the amount of volatile matter contained in the residual oil, and varies from practically 0 to 10 percent of the weight of the charge, depending upon the extent the charge

is blown. It is contended that vacuum process removes the oily and greasy materials from the residual oil and forms a brighter and cleaner looking blown asphalt. The more asphaltic the crude from which the residual oil is derived, the better will be the quality of the blown product, and the shorter the duration of the blowing process. Non-asphaltic petroleums will yield a good grade of blown asphalt if first subjected to a high temperature and pressure. The blowing reaction is exothermic and additional heating of the charge is not necessary once the air is admitted. Quite often the air rate needs to be reduced or the charge cooled by circulation through coils to prevent excessive temperature rise. The blowing can be carried out up to a temperature of about 600 ^{o}F., but often it is limited to lower temperatures because of the danger of cracking. Further, the blowing temperature should not be higher than the flash point of the charge, and preferably it should be 25 degrees lower. It can be seen that the temperature control and the effective use of air are very important considerations in the blowing process. Both of these considerations have been satisfactory dealt with in the continuous blowing processes now in operation. One type consists essentially of a vertical vessel with multiple air-jets passing through the base. The level of the asphalt is maintained constant, and the air supply is so regulated that the maximum use of the available oxygen is attained. With this type of plant, temperature control is greatly facilitated and

and uniform products are obtained.

The method by which the catalyst is introduced depends on the nature of the particular compound. Gaseous or readily vaporized agents can, of course, be supplied with the air, soluble salts can be injected in solution into the charge, and metallic and nonmetallic powders can be mixed thoroughly with a portion of the charge and then pumped into the still.

IV. EXPERIMENTAL PROGRAM

A series of tests was planned to determine the nature of products obtainable by straight air blowing of Redwater asphalt base stock and to evaluate the effect of phosphorus pentoxide as a "catalyst". The first series of these tests were designed to obtain basic data on the effect of air rate and blowing temperature upon straight air blowing, as well as to serve as a standard of comparison. It was decided to conduct tests at air rates of 55 and 75 cubic feet per minute per ton of charge and at temperatures of 465 and 525 ^{o}F.

The second series of tests were intended to show the effect of using phosphorus pentoxide as a "catalyst" in the blowing of the asphalt base stock. These tests were planned to evaluate the effect of 0.25%, 0.50% and 1.0% phosphorus pentoxide at the same air rates and temperatures employed in the first series. A supplementary test was also planned to evaluate the possibility of re-use of the residue expected from "catalytic" tests.

A third and final series of tests was planned to show whether different methods of dispersing the phosphorus pentoxide into the base stock would give different effects. The dispersing methods considered were mortar and pestle, mortar and pestle and the use of a 100 mesh screen as a suspending medium in the still, hand stirring, and use of a "dry" medium such as carbon tetrachloride.

V. EQUIPMENT

The pilot tests were conducted as a batch process in a conventional vertical cylindrical still as illustrated in Figures 1 and 2. The still proper was approximately 10 inches in diameter and 30 inches in height, and was mounted on a support made of 1 inch angle iron and $\frac{3}{4}$ inch diameter steel pipes. The charge was introduced at the top by removing the $\frac{1}{2}$ inch thick cover plate which was bolted to the still by four $\frac{1}{2}$ inch diameter bolts. Samples were withdrawn from one of the three sampling connections placed at different levels on the still. Attached to the bottom of the still was a fire box made of 16 gauge steel plate. Heat was applied directly by a 7 inch diameter ring type gas burner with automatic air control. Air was admitted into the charge through a spiral air coil set at the bottom of the still as shown in Figure 3. This air coil was made of $\frac{1}{4}$ inch o. d. mild carbon steel tubing, perforated with 7 holes 1/32 inch in diameter spaced 5 inches apart. These holes were all directed to the top of the still. A thermocouple well, also made of $\frac{1}{4}$ inch o. d. mild carbon steel tubing, was situated 4 inches from the bottom of the still. A $\frac{1}{4}$ inch vent line was provided to conduct the fumes outside the building. In addition, a connection was supplied for introduction of steam as a fire precaution. For all lines and connections, standard $\frac{1}{4}$ inch piping was used throughout.

Both the air rate and temperature of blowing were controlled, the former manually and the latter automatically. The flow was measured by a calibrated orifice, consisting of a 1/32 inch thick brass plate with a 1/16 inch diameter hole, mounted on a $\frac{1}{4}$ inch union. The temperature control was somewhat more refined. Two thermocouples were used, an iron-constantan thermocouple connected to a Leeds and Northrup portable potentiometer for actual temperature measurement, and a chromel-alumel thermocouple connected to a Brown millivoltmeter pyrometer controller for temperature control. The pyrometer actuated an on-off solenoid gas valve, thus controlling the rate of gas feed. The gas valve was on a by-pass of the main gas line, the latter providing the bulk of the gas required for heating the asphalt. The blowing temperature could be controlled within $\pm 3\ ^{o}F$.

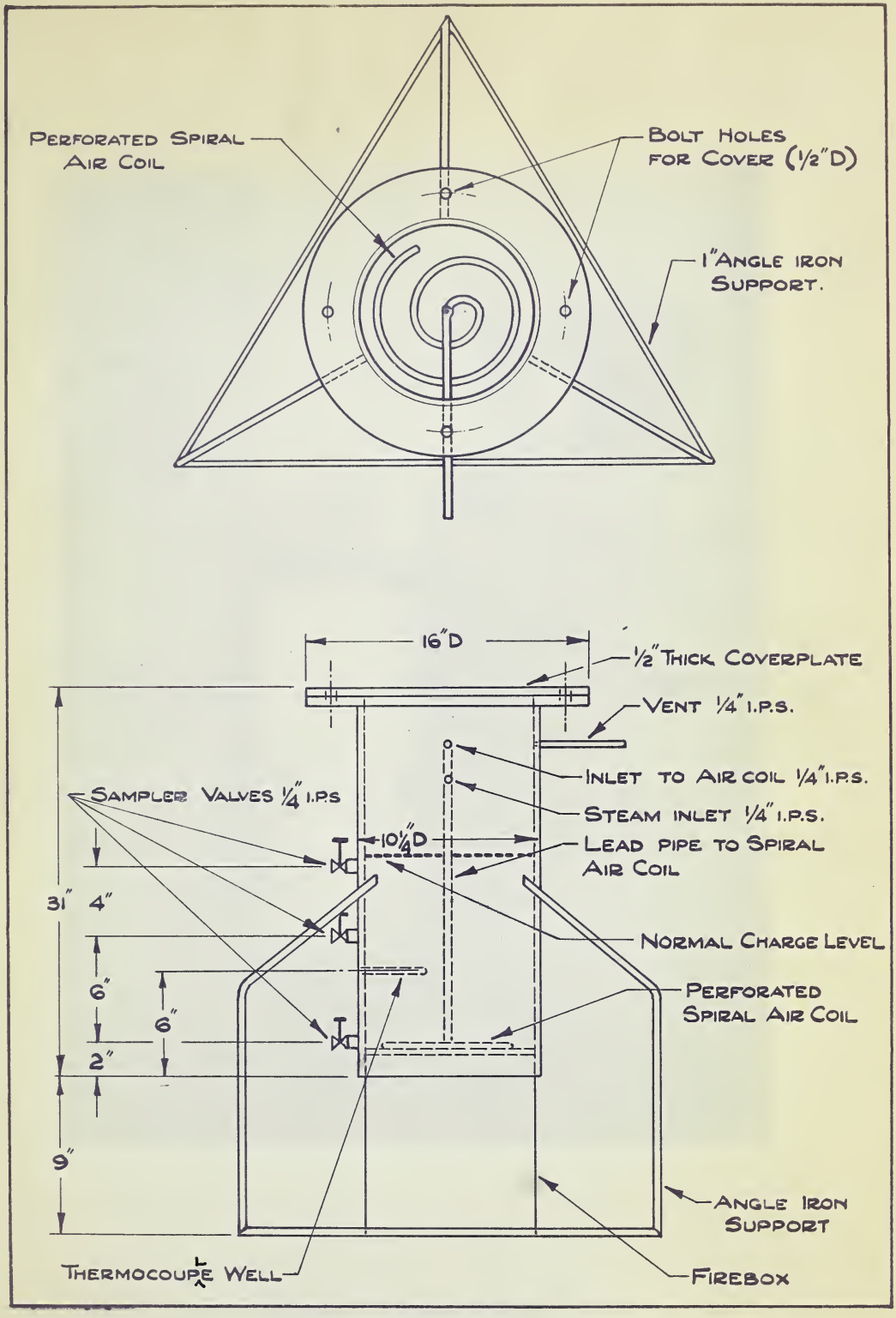

FIG.1. PILOT STILL.

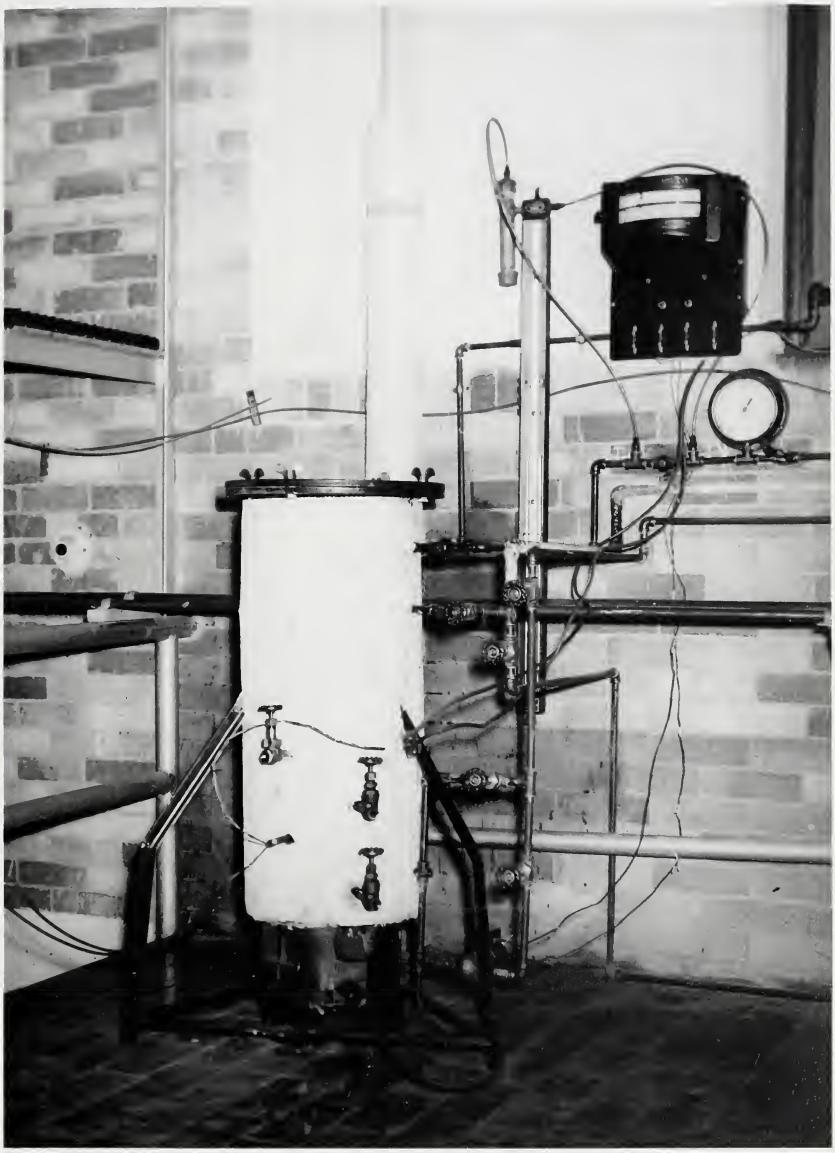

Fig. 2 Pilot Still

Fig. 3 Spiral Air Coil

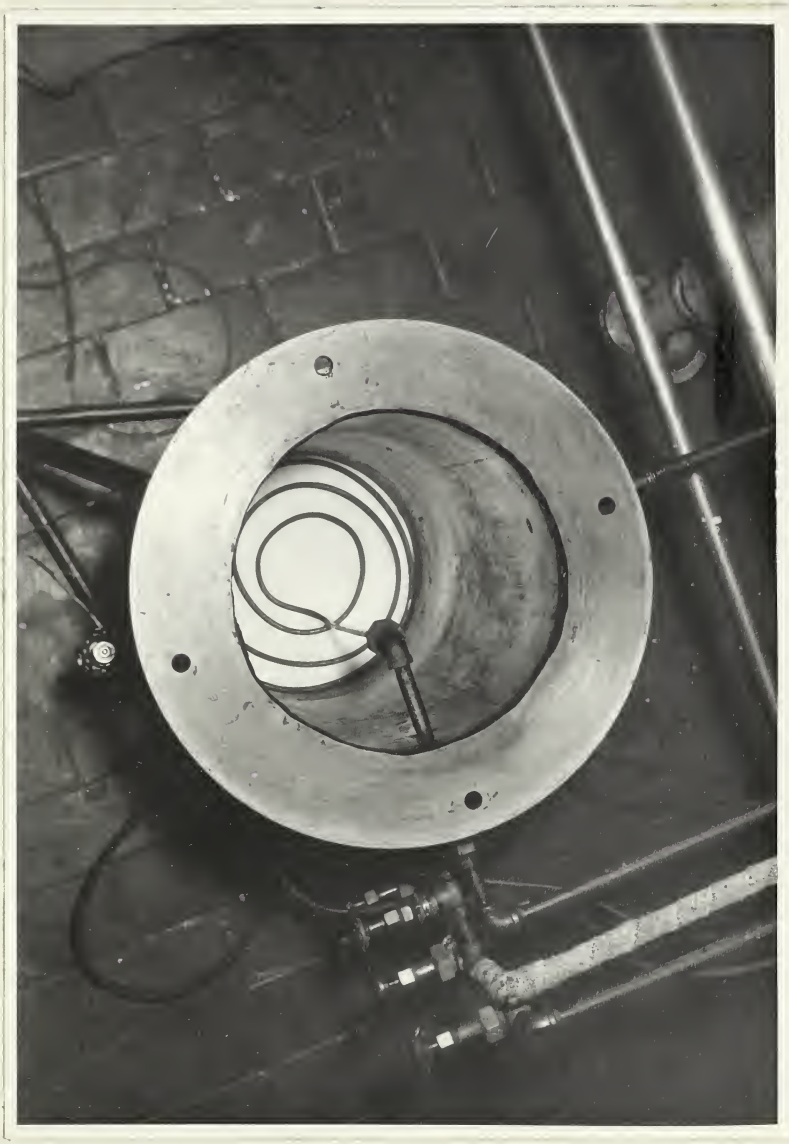

Fig. 4 Spiral Air Coil in Still

VI. EXPERIMENTAL PROCEDURE

For all the tests, approximately 30 pounds of asphalt base stock were weighed, heated until fluid and poured into the still. The cover plate of the still was replaced and the heating of the charge was continued in the still.

The first series of tests dealt with the straight air blowing of the base stock. As soon as the charge reached the blowing temperature, the stop-clock was started and the needle valve turned open immediately to admit air into the charge through a spiral air coil. The needle valve was adjusted so that the desired air rate was indicated by the readings on the Crosby pressure gauge and on the mercury manometer. At regular time intervals, an approximately one pound sample was withdrawn for testing. The blowing was continued until an asphalt with at least a 220 ^{o}F. softening point was obtained. At this point, the blowing was discontinued and the entire content of the still discharged. Before start of another test, the interior of the still was scraped free of any adhering asphalt and cleaned with varsol.

The second series of tests was to show the effect of using phosphorus pentoxide as a "catalyst" in air blowing the base stock. The phosphorus pentoxide was thoroughly dispersed in the base stock by use of a mortar and pestle and the resulting mixture air blown. The procedures used are described in detail below. The amount of pentoxide employed was varied from zero

up to one percent. A residue was found to be present in the still at the end of the "catalytic" tests. The presence of this residue raised the question whether the residue could be re-used in place of the phosphorus pentoxide and give similar results. The residue from one of the pentoxide test was carefully collected. One-half of this residue was dispersed into the base stock with exactly the same procedure as followed in the tests using the mortar and pestle type dispersions. The other half of the residue was analyzed for the percent of phosphorus pentoxide expressed as phosphorus pentoxide. The analytical procedures employed are described in Appendix 1.

The third series of tests was concerned with different methods of dispersing the phosphorus pentoxide into the base stock. In the dispersion by mortar and pestle, 10 percent of the charge to the still was withdrawn and heated to a temperature above 400°F. A weighed amount of phosphorus pentoxide was then added to the asphalt and ground in a mortar and pestle until a well dispersed paste was obtained. The air valve of the still was opened slightly to give the desired air rate and the dispersed paste added to the charge in the still; the charge in the still was already at its blowing temperature. The dispersion operation took approximately one-half hour and at no time was the mixture allowed to drop below 400°F.

In the dispersion by hand stirring, a similar procedure as with mortar and pestle was followed, but the pentoxide and

asphalt were stirred and agitated vigorously for one-half hour with a stirring rod made from a $\frac{1}{4}$ inch diameter steel rod. On appearance, the method did not produce as good a dispersion as by mortar and pestle. Many agglomerates of "catalyst" were visible after stirring.

When dispersing the pentoxide by mortar and pestle or by hand stirring, it was found important to add the pentoxide in small portions. When large portions were added, the pentoxide had a tendency to form large lumps, which could not be dispersed into the asphalt.

Phosphorus pentoxide is highly hygroscopic and in the presence of air it will readily absorbed enough moisture to form at least a water film around each pentoxide particle. Since water and asphalt are immiscible, it was believed that with this water film the pentoxide particles may not react as readily with the asphalt and tend instead to agglomerate. For this reason, it was decided to investigate the possibility of first immersing the phosphorus pentoxide in carbon tetrachloride and then adding this mixture to the asphalt charge. The required amount of phosphorus pentoxide was weighed in a beaker and immediately covered by 300 ml of carbon tetrachloride. With the charge at the blowing temperature, the needle valve was opened to the desired air rate and the pentoxide-carbon tetrachloride mixture was poured into the still slowly to prevent foaming as the carbon tetrachloride rapidly vaporized off.

As was stated earlier, a certain amount of residue was present in the still at the end of each pentoxide test. It was believed that since some of the larger particles of pentoxide may have settled out during the blowing, the contact surface area between the pentoxide and asphalt may have been reduced. Therefore, in the dispersion by mortar and pestle and screen, a 100 mesh brass screen was placed $2\frac{3}{4}$ inches from the still bottom to support any pentoxide particles that tended to settle out during the blowing. The actual dispersion procedure was the same as that for the mortar and pestle.

The original base stock and samples from all tests were examined for the following properties:

Softening point (Ring and Ball)

Penetration at 32 °F., 200 grams, 60 seconds

77 °F., 100 grams, 5 seconds

100 °F., 100 grams, 5 seconds

115 °F., 50 grams, 5 seconds

Saybolt Furol viscosity at 210 °F., 250 °F., 275 °F.

Ductility at 77 °F.

Specific gravity at 77 °F.

Solubility in carbon tetrachloride

Methods of the American Society of Testing Materials (3) were followed in making the tests. The designations are given in Appendix II.

In addition to the above tests, samples of a straight

blown and a pentoxide blown test covering the softening point range from 107 °F. to 210 °F. were analyzed for the percent asphaltenes, resins and oily constituents. The procedures employed for the analyses were essentially the method proposed by O. G. Strieter (39). The slight modifications are presented in Appendix III. The mean molecular weights of the three fractions were determined by a cryoscopic method using water-saturated benzene as the solvent. The procedure of Hoiberg, Hougen and Zapata (17) was employed. The details are presented in Appendix IV.

VII. EXPERIMENTAL RESULTS

The results of the examination of the Redwater asphalt base stock are presented in Table I. This table indicates that the base stock has a softening point of 107 °F., a penetration of 148 at 77 °F., a viscosity of 540 seconds at 210 °F., and a flash point greater than 350 °F. Table II to XIII inclusive present the results of each pilot test. These tables are headed by the operating conditions of the test, such as weight of charge, air rate, blowing temperature, barometric pressure, the amount of phosphorus pentoxide and the method of dispersing it. The accumulative blowing time at the instant of sampling is shown in the first column. The sample number is in column two. The results of the tests of the samples for softening point, penetration, Saybolt Furol viscosity, ductility, specific gravity, solubility in carbon tetrachloride, and fractional composition follow in the remaining columns.

Tables II to IV inclusive present the results of the straight blown tests conducted under different operating conditions. Tables V to IX inclusive offer the results of the tests with phosphorus pentoxide dispersed by mortar and pestle. The first three tables of pentoxide blown tests show the effect of varying the percent of pentoxide with the blowing temperature and air rate both constant, and the remaining two tables show the effect of using a different blowing temperature and a different air rate with the percent of pentoxide constant. The results of

re-using the residue from a pentoxide test are tabulated in Table X. Tables XI, XII, and XIII show the effect of dispersing the pentoxide by hand stirring, by the use of carbon tetrachloride, and by mortar and pestle and screen respectively.

Table I

PROPERTIES OF VACUUM REDUCED REDWATER ASPHALT BASE STOCK

Softening point (ring and ball)		- 107.0 °F
Penetration at	32 °F, 200 gm, 60 sec	- 24
	77 °F, 100 gm, 5 sec	- 148
	100 °F, 100 gm, 5 sec	- too soft
	115 °F, 50 gm, 5 sec	- too soft
Saybolt Furol viscosity at	210 °F	- 540 sec
	250 °F	- 138 sec
	275 °F	- 89 sec
Ductility at 77 °F		- 150 plus
Specific gravity 77 °F/77°F		- 1.007
Solubility in carbon tetrachloride		- 99.60%
Float test at 122 °F		- 343 sec
Flash point (Cleveland open cup)		- 350 °F plus
Asphaltenes,	percent by weight	- 18.1
	mean molecular weight	- 1299
Resins,	percent by weight	- 43.4
	mean molecular weight	- 601
Oily Constituents,	percent by weight	- 38.5
	mean molecular weight	- 525

Table II

BLOWING OF REDWATER ASPHALT BASE STOCK

Test No. 1

Charge 30.8 lb
Phosphorus pentoxide - 0%

Blowing temperature - 465 °F
Barometric pressure - 70.3 cm
Air rate - 55 cu ft/min-ton charge

Blowing time hrs-min	Cut no.	S.P. (R&B)	Penetrations 32°F	77°F	100°F	115°F	S. F. Viscosity 210°F	250°F	275°F	Duct. 77°F	S.G. 77/77°F	% sol. CCl_4
0-0	0	107.0	24	148			540	138	89		1.007	99.60
0-15	1	109.2	21	118			596	138			1.005	99.91
0-30	2			109								
0-45	3			101								
1-0	4	113.2		86			726	174	89	100+	1.004	99.75
1-15	5		17	84								
1-36	6			82								
1-45	7			79								
2-0	8	119.0		75			952	223	108	100+	1.008	99.75
2-15	9		15	68								
2-30	10	120.5		62								
2-45	11			55								
3-0	12	123.5		56			1260	251		100+	1.005	99.82
3-19	13		13	54								
3-30	14	125.5		51	182							
3-45	15			48					161			
4-0	16	127.1		46		249		307		100+	1.006	
4-5	17	129.5		42				381		90.0	1.010	99.87
5-7	18	136.0		32		130		554		25.5		
6-15	19	145.5	9	25	74	82		1105	359	10.0		
7-4	20	155.0		21	56	60				4.8		
8-20	21	172.9		14	38	38			1200	3.0	1.017	99.87
10-5	22	209.0	7	10	22	26				3.0		
11-40	23	235.0	7	8								

Table III

BLOWING OF REDWATER ASPHALT BASE STOCK

Test No. 2

Charge - 30.0 lb
Phosphorus pentoxide - 0%

Blowing temperature - 525°F
Barometric pressure - 70.4 cm
Air rate - 55 cu ft/min-ton charge

lowing time rs-min	Cut no.	S.P. (R&B)	Penetrations 32°F	77°F	100°F	115°F	S. F. Viscosity 210°F	250°F	275°F	Duct. 77°F	S.G. 77/77°F	% sol. CCl_4	Asphaltenes %	mol. wt.	Resins %	mol. wt.	Oily Constituents %	mol. wt.
0-11	1	109.5	20.0	124			615	146	90	100+			18.7	1592	40.9	609	40.4	529
0-50	2	119.0					951						22.8	1977	42.5	623	34.7	609
1-20	3	127.0	12.0	42	189	273	1460	320	143	100+	1.003	99.73						
1-50	4	136.0								23.0			31.1	2342	37.7	661	31.2	626
2-20	5	145.5				81		1102		9.2			33.1	2469	31.0		35.9	621
3-0	6	155.0	9.0	20	53	59		1700	488	4.0								
3-50	7	173.0											38.2	2803	28.9	758	32.9	628
4-0	8	185.5	7.0	11	28	30				2.5	1.018	99.83						
5-0	9	200.0	7.0	8	19	25				2.6								
5-20	10	209.0											39.6	3244	27.0	865	33.4	670
6-0	11	225.0	6.0	7	14	22				2.5	1.022	99.77						

Table IV

BLOWING OF REDWATER ASPHALT BASE STOCK

Test No. 3

Charge - 28.9 lb
Phosphorus pentoxide - 0%

Blowing temperature - 525 °F
Barometric pressure - 70.4 cm
Air rate - 75 cu ft/ min-ton charge

Blowing time hrs-min	Cut no.	S.P. (R&B)	Penetration at 77°F
1-0	1	136.0	30
2-0	2	166.5	15
3-0	3	208.2	8
4-0	4	240.0	7
5-0	5	270.0	6

Table V

BLOWING OF REDWATER ASPHALT BASE STOCK

Test No. 4

Charge - 27.2 lb
Phosphorus pentoxide - 0.25%
Dispersion method - mortar and pestle
Blowing temperature - 525 °F
Barometric pressure - 70.6 cm
Air rate - 55 cu ft/min-ton charge

Blowing time hrs-min	Cut no.	S.P. (R&B)	Penetrations 32°F	77°F	100°F	115°F	S. F. Viscosity 210°F	250°F	275°F	Duct. 77°F	S.G. 77/77°F	% sol. CCl_4
1-0	1	117.0	17.2	90			875	180	84			
2-0	2	123.5	15.0	61			1351	239		100+	1.012	99.35
2-57	3	133.5	13.0	40	160				189	60.0		
4-10	4	144.5	11.2	28	86	90		1080	330	10.5	1.015	99.54
6-4	5	172.0	9.0	17	37	41			1447	3.5	1.019	99.57
7-0	6	202.5	7.4	13	25	24				2.0		
8-5	7	238.0	6.5	9	17	21					1.029	99.59

Table VI

BLOWING OF REDWATER ASPHALT BASE STOCK

Test No. 5

Charge - 29.1 lb
Phosphorus pentoxide - 0.5 %
Dispersion method - mortar and pestle
Blowing temperature - 525 °F
Barometric pressure - 70.8 cm
Air rate - 55 cu ft/min-ton charge

Blowing time hrs-min	Cut no.	S.P. (R&B)	Penetrations 32°F	77°F	100°F	115°F	S. F. Viscosity 210°F	250°F	275°F	Duct. 77°F	S.G. 77/77°F	% sol. CCl_4
1-0	1	109.5	20.4	145			606	150				
2-0	2	112.5	19.3	123			681		84	83.0	1.005	99.73
3-0	3	117.8	17.6	92			964	215				
4-8	4	131.0	13.9	48	166	232		420		70.0		
5-0	5	145.0	12.0	32	78			1251	361	10.6	1.012	99.79
6-0	6	157.5	10.6	23		60			856	4.2		
6-45	7	167.5	9.8	20	41				1600	3.0	1.018	99.76
8-15	8	197.5	8.2	14		32						
9-5	9	221.0	7.5	14	24					1.5	1.023	99.72
10-0	10	230.0	7.1	11		25						

Table VII

BLOWING OF REDWATER ASPHALT BASE STOCK

Test No. 6

Charge - 29.1 lb
Phosphorus pentoxide - 1.0%
Dispersion method - mortar and pestle
Blowing temperature - 525°F
Barometric pressure - 70.8 cm
Air rate - 55 cu ft/min-ton charge

Blowing time hrs-min	Cut no.	S.P. (R&B)	Penetrations 32°F	77°F	100°F	115°F	S. F. Viscosity 210°F	250°F	275°F	Duct. 77°F	S.G. 77/77°F	% sol. CCl_4	Asphaltenes %	mol. wt.	Resins %	mol. wt.	Oily Constituents %	mol. wt.
1-0	1	110.0		136									20.3		40.7	605	39.0	584
1-30	2	111.0	22.0				655			100+		99.58						
2-0	3	111.0		136				156										
2-30	4	112.5	20.5	126				172					21.4	1287	40.6	608	38.0	587
3-0	5	115.0		116														
3-30	6	116.0	20.1				877		95									
4-0	7	117.5		94			1001	218		80.0	1.014		23.1	1395	39.9	615	37.0	
	8	126.1	17.1	60	197				160			99.70						
5-0	9	130.0	17.0	49		247												
5-30	10	135.0	15.6	41	140			610	245	53.0			29.4	1610		634		650
6-0	11	138.6	14.3	36		139		950		13.3	1.010	99.75						
	12	146.5	14.0	34	84													
6-40	13	156.0	12.1	32		94			851	4.5			33.6	2001	33.2	690	33.2	675
7-0	14	162.0	12.1	28	61	78				4.0								
9-40	15	217.0	9.8	18	32	34				2.6								
10-20	16	233.5	9.0	15	30	30					1.021	99.75	43.0	2776	25.4	944	31.6	760

Table VIII

BLOWING OF REDWATER ASPHALT BASE STOCK

Test No. 7

Charge	- 30.0 lb	Blowing temperature	- 465 °F
Phosphorus pentoxide	- 0.5%	Barometric pressure	- 70.3 cm
Dispersion method	- mortar and pestle	Air rate	- 55 cu ft/min-ton charge

Blowing time hrs-min	Cut no.	S. P. (R&B)	Penetration at 77°F
1-0	1	109.0	150
2-0	2	110.0	141
3-0	3	112.5	
4-0	4	119.0	80
5-0	5	129.0	53
6-0	6	135.1	43
6-40	7	146.1	33
8-5	8	163.0	24
9-20	9	180.0	18
10-0	10	192.0	16
11-0	11	213.0	15
12-0	12	244.3	13

Table IX

BLOWING OF REDWATER ASPHALT BASE STOCK

Test No. 8

Charge	- 30.1 lb	Blowing temperature	- 525 °F
Phosphorus pentoxide	- 0.5%	Barometric pressure	- 70.1 cm
Dispersion method	- mortar and pestle	Air rate	- 75 cu ft/min-ton charge

Blowing time hrs-min	Cut no.	S. P. (R&B)	Penetration at 77°F
1-0	1	115.1	105
2-0	2	127.0	55
3-0	3	144.1	32
4-0	4	170.0	20
5-0	5	204.2	14
6-0	6	239.9	12

Table X

BLOWING OF REDWATER ASPHALT BASE STOCK

Test No. 9

Charge - 29.3 lb
Phosphorus pentoxide - 300 gm residue (8.59% P_2O_5)
- 0.19%
Dispersion method - mortar and pestle

Blowing temperature - 525 °F
Barometric pressure - 71.1 cm
Air rate - 55 cu ft/min-ton charge

Blowing time hrs-min	Cut no.	S.P. (R&B)	Penetrations 32°F	77°F	100°F	115°F	S. F. Viscosity 210°F	250°F	275°F	Duct. 77°F	S.G. 77/77°F	%sol. CCl_4
0-20	1	110.2	22.1	134			648	186	83	100+		
0-40	2	113.4	20.8	95			671			100+	1.007	99.57
1-0	3	118.6	17.8	68			1003	248	114	100+		
1-40	4	127.5	14.4	43		259				80.0		
2-20	5	134.8	11.5	35	125			549	233	19.7		
2-40	6	146.0	10.5	26	68	80		1150	351	7.5	1.014	99.57
4-40	7	182.8	8.0	15	29	33				3.0		
5-30	8	198.0	7.9	13	23	27					1.019	99.64
6-0	9	213.0	7.0	11	20	24					1.022	99.59

Table XI

BLOWING OF REDWATER ASPHALT BASE STOCK

Test No. 10

Charge - 28.9 lb
Phosphorus pentoxide - 1.0%
Dispersion method - hand stirring
Blowing temperature - 525 °F
Barometric pressure - 70.1 cm
Air rate - 55 cu ft/min-ton charge

Blowing time hrs-min	Cut no.	S.P. (R&B)	Penetrations 32°F	77°F	100°F	115°F	S. F. Viscosity 210°F	250°F	275°F	Duct. 77°F	S.G. 77/77°F	% sol. CCl_4
0-11	1	106.0	22.0				595				1.007	99.68
1-0	2	107.0		140			611	190	106			
2-0	3	112.0		97				222		100+	1.003	
3-0	4	116.0		77			842	226		80.0		
4-0	5	119.0	17.0	62			991				1.007	99.45
4-30	6	123.8		54					148	74.5		
5-0	7	127.5		42	165	169		395		67.5	1.003	
5-30	8	132.5		37	115			502		62.5		
6-0	9	144.0		34		97		1009		9.6		99.53
	10	146.1	12.0	34		85		1126	362		1.009	
6-30	11	148.2		29	72	80						
7-0	12	151.4		26				1430	512			
7-30	13	154.0		26		65						99.52
8-0	14	162.0	11.2	24	48	55				4.0	1.017	
9-40	15	210.0	9.2	15	32	33				3.5		

Table XII

BLOWING OF REDWATER ASPHALT BASE STOCK

Test No. 11

Charge - 29.9 lb
Phosphorus pentoxide - 1.0%
Dispersion method - carbon tetrachloride
Blowing temperature - 525 °F
Barometric pressure - 71.0 cm
Air rate - 55 cu ft/min-ton charge

Blowing time hrs-min	Cut no.	S.P. (R&B)	Penetrations 32°F	77°F	100°F	115°F	S. F. Viscosity 210°F	250°F	275°F	Duct. 77°F	S.G. 77/77°F	% sol. CCl_4
1-0	1	114.0	24.5	91	300-		739	195	91	99.0	1.007	99.52
2-0	2	138.5	14.4	39	89	144		811	295	14.0	1.014	99.14
3-0	3	171.4	10.1	19	38	44				2.5	1.016	99.21
4-0	4	218.0	8.9	16	25	25				2.0	1.029	99.12
5-0	5	240.0	8.2	14	23	24				1.5		
5-45	6	252.5	6.0	11	19	17				0.5		

Table XIII

BLOWING OF REDWATER ASPHALT BASE STOCK

Test No. 12

Charge - 30.6 lb
Phosphorus pentoxide - 1.0%
Dispersion method - mortar and pestle and screen
Blowing temperature - 525 °F
Barometric pressure - 71.5 cm
Air rate - 55 cu ft/min-ton charge

Blowing time hrs-min	Cut no.	S.P. (R&B)	Penetrations 32°F	77°F	100°F	115°F	S. F. Viscosity 210°F	250°F	275°F	Duct. 77°F	S.G. 77/77°F	% sol. CCl_4
1-0	1	110.2	20.9	135			649	195	89		1.005	99.55
2-0	2	117.4	19.0	94			981			100+		
3-0	3	122.1	17.5	71	219			292	112	76.0		
5-0	4	134.2	15.3	44	142	220		500	220	48.6	1.010	99.74
6-0	5	158.0	12.2	27	63	83			1040	5.0	1.017	
8-0	6	188.5	10.2	20	39	47				3.8		99.71
9-0	7	211.0	9.7	18	34	35				3.5	1.020	99.63
10-40	8	253.0	9.0	15	29	28						

VIII. DISCUSSION OF RESULTS

By various air blowing procedures on Redwater asphalt base stock, a very wide range of closely controlled products may be obtained. Generally speaking, the blown product is harder (lower penetration), heavier, lower in ductility, higher in viscosity, and higher in softening point than before the blowing; the extent of the change in properties being dependent upon the reaction time (time of blowing), the temperature of blowing, the air rate, the use of "catalyst" (and presumably, the method of dispersing it). It is convenient to illustrate the effect of time, temperature and air rate on the physical properties by reference to the softening point which perhaps is the single most important physical property of an asphalt. For this reason, all test results are related to the softening point.

Series 1 - Straight Air Blowing

Effect of Temperature and Air Rate on Reaction Time

In the case of the tests conducted without the use of phosphorus pentoxide, the effect of temperature and air rate on the reaction time is presented in Figure 5, the progress of the reaction being measured by the change in the softening point. The data indicate that increasing the blowing temperature from 465 °F. to 525 °F. reduces the time required to reach a 220 °F. softening point asphalt to almost one-half. A similar effect occurs when the blowing temperature is fixed and the air rate increased.

Effect of Temperature and Air Rate on Penetration, Viscosity, Ductility, Softening Point Relationships

Temperature and air rate have substantially the same effect upon the other physical properties of the asphalt. This is indicated by the fact that the relationships between the other properties and the softening point (chosen as the reference property) are changed very little by either temperature or air rate. Figures 6 to 11 inclusive indicate only a very slight effect of the blowing temperature, within the range of 465 to 525°F., on the penetration-softening point, viscosity-softening point, and ductility-softening point relationships. Figure 7 shows the corresponding small effect of the air rate, within the range 55 to 75 cubic feet per minute per ton of charge, on the penetration-softening point relationship. It is concluded that increasing the blowing temperature or the air rate, or both, does not change the properties of the final asphalt with relation to a given softening point, but it does, however, decrease the reaction time markedly.

Series 2 - Air Blowing with Phosphorus Pentoxide "Catalyst"

Effect of Phosphorus Pentoxide on Reaction Time

In the tests conducted with phosphorus pentoxide as an addition agent, the results indicate a retarding effect on reaction rate or an increase in the reaction time. The degree by which the reaction time is increased is dependent on the

amount of phosphorus pentoxide. This effect is illustrated in Figure 12. While it requires approximately 6 hours to produce a 230 °F. softening point asphalt with no "catalyst", more than 10 hours are necessary to produce the same softening point in the presence of 1.0 percent phosphorus pentoxide. From the industrial point of view, this increase in reaction time, while it would decrease capacity and increase air requirements, is not entirely undesirable since it would allow better control and therefore permit a better product. It is also interesting to note that the phosphorus pentoxide has a retarding effect on the reaction rate only in the early stages of the blowing. In the later stages, the reaction rate appears to be nearly constant at a value (measured in terms of rate of change of softening point) of approximately 24 Fahrenheit degrees per hour. This value is seen to be independent of the amount of phosphorus pentoxide employed, at least up to one percent.

Effect of Temperature and Air Rate

As with the tests conducted without phosphorus pentoxide, the increase in the blowing temperature and the air rate have substantially the same effect; that is, as illustrated in Figures 13 and 14, the reaction time is reduced but the penetration-softening point relationship remains unchanged. However, it is interesting to compare Figure 13 with Figure 5. It may be seen that the time required to reach a given softening point asphalt may be reduced either by increasing the blowing temperature

or by increasing the air rate. This degree of time reduction is different for the straight blown and pentoxide blown tests, although in both cases the operating variables are the same. If curve 2 is compared to curve 1 in the respective graphs, an increase in the blowing temperature in the pentoxide blown test produces a smaller decrease in reaction time than in the straight blown test. Similarly, comparing curve 3 to curve 2, an increase in the air rate in the pentoxide blown test gives a much greater decrease in reaction time than in the straight blown test. It may be observed that at the early stages of the blowing process, the reaction time curves for the pentoxide blown tests show a greater curvature than do those for the tests conducted in the absence of "catalyst".

Effect of Phosphorus Pentoxide on Penetration, Viscosity, Ductility, Softening Point Relationships

With the addition of small amounts of phosphorus pentoxide, the relationships between the other physical properties of the blown asphalt and the softening point are changed substantially. Figures 15 to 18 inclusive indicate that the penetration of the blown asphalt is increased appreciably for a given softening point. Under similar blowing conditions and with the same dispersion method, this penetration increase is approximately proportional to the amount of pentoxide added, at least up to one percent. As indicated in the 1.0 percent phosphorus pentoxide curve in Figure 16, the increase is of the order of 10 penetration units at 77 °F.

for a 220 °F. softening point asphalt. Based on the penetration of a straight blown product of the same softening point, this would represent approximately a 130 percent increase in penetration number. At lower softening points, this increase in penetration number is considerably less.

Figure 19 shows the effect of phosphorus pentoxide on the viscosity-softening point relationship of the blown asphalt. For a given softening point, the viscosity is increased with increasing percentages of phosphorus pentoxide used. Because the viscosity apparatus was built to operate only at 210 °F. or lower, it was difficult to keep the temperature of the test samples constant at higher temperatures. Hence considerable trouble was encountered in determining viscosities at 250 °F. and 275 °F. Several trials had to be made on each sample before a suitable check could be obtained. It was intended initially to determine the viscosity at 325 °F. or at a sufficient high temperature to test 220 °F. softening point asphalt. However, due to the difficulty encountered at the lower temperatures, this was not possible.

The pentoxide blown asphalts were tested for their ductilities at 77 °F. and the results are shown in Figure 20. Asphalts blown to a softening point less than 130 °F. with 0.5 and 1.0 percent phosphorus pentoxide do show a much lower ductility than those blown with 0.25 and zero percent phosphorus pentoxide. Blown asphalts with softening points between 130

and 140 °F. are in the "critical zone". The ductility changes in this zone from 80 to approximately 10 cms. Because of the nature of the test and insufficient test data, the curves in this zone are considered not too satisfactory. Blown asphalts with softening points greater than 140 °F. show approximately the same ductility whether they were blown with or without phosphorus pentoxide.

For blown asphalts with softening points less than 130 °F., the data are inconclusive, but seem to indicate a ductility decrease with increasing amounts of phosphorus pentoxide. It appears probable that the phosphorus pentoxide requires some time before it completely reacts with the asphalt and hence at the early stages of the blowing, the ductility may decrease due to the entrainment of unreacted pentoxide.

Effect of the Pentoxide Residue

As mentioned earlier, in air blowing the asphalt base stock in the presence of phosphorus pentoxide, a certain amount of residue was found present in the bottom of the still at the end of the test. This residue had the appearance od coke and did not dissolve readily in carbon tetrachloride or in benzene. This hard gritty residue may have been formed either by the oxidation of the asphalt by particles of phosphorus pentoxide or polymerizing reactions between the asphalt and the pentoxide. In the initial pentoxide tests, the appearance of this residue raised some doubts as to the reproducibility of the tests.

However, further tests with the same percentage of phosphorus pentoxide made under identical operating conditions yielded the same penetration-softening point relationship and removed these doubts.

The presence of the residue also raised the question whether the residue could be re-used in place of phosphorus pentoxide to produce the same effect on the penetration-softening point relationship. If this residue could be re-used, it would mean a large saving in cost in commercial operations.

From a 0.5 percent pentoxide test, 600 grams of the residue were recovered. This residue was analyzed and found to contain 8.59 percent phosphorus expressed as phosphorus pentoxide; the remainder was assumed to be carbonaceous material. Using a charge of 30.3 pounds or 13,800 grams, 69 grams of phosphorus pentoxide were dispersed into the base stock. From the residue, 51.6 grams of phosphorus pentoxide were accounted for. This meant that only 17.4 grams or 25.4 percent of the pentoxide added reacted with the asphalt, the remaining 51.6 grams or 74.6 percent appeared in the residue.

Three hundred grams of the recovered residue containing 25.8 grams of phosphorus expressed as phosphorus pentoxide were dispersed into 29.3 pounds or 13,300 grams of base stock. Theoretically, this should be equivalent to an addition of 0.19 percent phosphorus pentoxide. Some of the phosphorus may not have been present as phosphorus pentoxide and accordingly

the value may be lower than 0.19 percent. Very little trouble was encountered in the dispersion. At the end of the test, only a small amount of residue was present in the still. Unfortunately, this residue was not recovered and hence it was not possible to analyze for phosphorus pentoxide. The results of this test on the re-use of the residue are presented in Figure 12, and Figures 15 to 20 inclusive along with those of the normal pentoxide blown tests.

The effect of the residue on the reaction time is illustrated in Figure 12. The data indicate the pentoxide residue to be only 1/4 to 1/3 as effective in increasing the reaction time as phosphorus pentoxide. As with the pentoxide tests, the reaction time curve of the residue test exhibits a constant slope at the later stages of the blowing process.

With the use of the pentoxide residue a favorable shift in the penetration-softening point relationship is indicated. As shown in Figures 15 to 18 inclusive, the penetration increase for a given softening point is about what would be expected with the same percentage of fresh phosphorus pentoxide. It appears that the pentoxide residue is as effective as the phosphorus pentoxide itself. In fact, it seems that the use of the pentoxide residue has an advantage since the residue is non-hygroscopic and it does not show the same tendency to agglomerate during dispersion. The residue reduces the reaction time as compared to the phosphorus pentoxide,

and therefore it will increase capacity and decrease air requirements. In addition, only a small amount of residue was found present in the bottom of the still after the test. This means that the "catalyst" handling, dispersion, and cleaning problems will be greatly simplified and reduced. In commercial operations, these factors are very important.

As illustrated in Figures 19 and 20, the use of the residue has the same effect as phosphorus pentoxide in the viscosity-softening point and ductility-softening point relationships. Comparing the residue curve to the zero percent pentoxide curve, the viscosity (referred to a given softening point) is increased and this increase approximates very closely the increase produced by 0.25 percent phosphorus pentoxide. However, the ductility curve of the residue is almost identical with the curve obtained with zero percent phosphorus pentoxide.

Effect of Phosphorus Pentoxide on Asphaltenes, Resins and Oily Constituents

In attempting to explain the changes which take place when the asphalt base stock was air blown, the fractional composition of the asphalt was considered. Samples of a straight blown and a pentoxide blown test covering the softening point range from 107 °F. to 210 °F. were analyzed and separated into the three major fractions: asphaltenes, resins and oily constituents. It is well to remember, however, that although each fraction has general characteristics which are distinctive,

its properties and yields vary with the source and method of analysis. For this reason, correlations of fractional composition with physical properties and service behavior which hold for asphalts from different crude oils are difficult to develop.

Figure 21 shows the change in the fractional composition of the asphalt base stock as it is air blown with and without the use of phosphorus pentoxide. The air blowing increases the asphaltenes from about 20 to 40 percent and at the same time reduces the resins from approximately 45 to 25 percent. Only a slight change in the proportion of oily constituents occurs. The fractional compositions of the straight blown and the pentoxide blown asphalts are found to be almost identical, at least within two percent. This is consistent with Hoiberg's observations (15). Perhaps this two percent difference is sufficient to cause the difference in the physical properties of the straight blown and pentoxide blown asphalts. However, more data are needed on blown asphalts produced from different base stocks and with different addition agents before the behavior of the straight blown and pentoxide blown asphalts can be related to their fractional composition.

The properties of the asphaltenes, resins and oily constituents were examined and found to be consistent with those reported in the literature (23, 27, 28, 29, 33, 36, 40). The asphaltenes were dark brown to black powdery solids. Upon heating, they did not melt but sintered and fused and

finally decomposed into a compact, hard coke-like material. They were soluble in benzene, chloroform, carbon tetrachloride, and carbon disulphide, but insoluble in alcohol, ether, acetone, and petroleum naphtha. The asphaltenes were considered to be the substances that impart "body" and "hardness" to the asphalt.

The resins were low melting point solids. They were reddish brown substances which were soluble in light petroleum naphtha, benzene, chloroform, carbon tetrachloride, and carbon disulphide, but only sparingly soluble in hot or cold acetone. The resins gave the asphalt its ductility and tensile strength.

The oily constituents at room temperature exhibited the properties of a viscous liquid. They were light yellow in color. They differed from resins in that they remained dissolved in light petroleum naphtha after treatment with anhydrous alumina or adsorbent clay, whereas the resins were adsorbed. The oily constituents had the appearance of a heavy lubricating oil. The primary function of the oily constituents was to act as a dispersing medium for the asphaltenes and resins. As a general rule, the softer the asphalt, the higher will be its content of oily constituents.

Besides examining the properties of the asphaltenes, resins and oil constituents and determining how the percent of each varied on air blowing, the mean molecular weights of the three fractions were determined. Figure 22 shows that the mean molecular weight of the fractions increases markedly

with air blowing. The mean molecular weight of the asphaltenes increases from about 1000 to 3000, the resins from approximately 600 to 900, and the oily constituents from 500 to 700. Since the molecular weights were determined by a cryoscopic method, the accuracy of the results was dependent on the amount of the fraction used and the accuracy by which the temperature depression may be measured. The amount of the fraction was limited by the size of the Soxhlet extractor available for separating the asphalt into the various fractions. The molecular weights reported are considered accurate within ±15 percent for the asphaltenes, ±6 percent for the resins, and ±5 percent for the oily constituents. Therefore referring to Figure 22, it can be stated that likely the pentoxide blowing forms asphaltenes with a lower mean molecular weight and oily constituents with a higher mean molecular weight than that produced by straight air blowing. The molecular weights of the resins are quite similar whether they are formed by straight air blowing or "catalytic" blowing. Hoiberg (15) stated that in the pentoxide tests, the increased penetrations may perhaps be due to the formation of asphaltenes of higher molecular weight than that produced by straight air blowing. However, he did not report any actual experimental data. As shown in this investigation and illustrated in Figure 22, asphaltenes of lower mean molecular weight are produced by "catalytic" blowing than by straight air blowing.

Series 3 - Air Blowing with Phosphorus Pentoxide Dispersed by Different Methods

Effect of Dispersion Method on Reaction Time

The method of dispersing the phosphorus pentoxide in the asphalt was found to be comparable in importance to the amount of phosphorus pentoxide used. Figure 23 illustrates the effect of different dispersion methods on the reaction time. It seems that dispersion by use of carbon tetrachloride produces, except at the very early stages of blowing, a higher reaction rate compared with that of the straight blown test. That is, the use of carbon tetrachloride decreases the reaction time required to produce a given softening point asphalt. This is contrary to what is expected since the earlier investigations indicate that the pentoxide, when dispersed by mortar and pestle, increases the reaction time. This decrease is believed due to the action of the carbon tetrachloride. Although practically all the carbon tetrachloride is flashed off immediately, possibly the slightest amount remaining in solution is sufficient to speed up the reaction. It is also possible that this reaction rate increase may be due to the action of by-products formed from carbon tetrachloride. It is known that at high temperatures, carbon tetrachloride will form phosgene. While dispersing the phosphorus pentoxide into the asphalt by carbon tetrachloride, extreme precautions are required. When the pentoxide-carbon tetrachloride mixture is added to the hot asphalt in the still, excessive foaming takes place. The fumes that are given off

are very sharp, penetrating and extremely poisonous.

Dispersion of phosphorous pentoxide by hand stirring, mortar, pestle and screen produce apparently similar effects on the reaction rate. The reaction rate is decreased and hence a longer reaction time is required to form a given softening point asphalt. The reaction time is greatest when the pentoxide is dispersed by hand stirring. As the method of dispersion is improved by use of a mortar and pestle and finally by use of a mortar, pestle and screen, the reaction time is decreased accordingly. This observation contradicts the observation that the increase in reaction time is due to the effect of the phosphorus pentoxide. If this were so, it might be expected that as the method of dispersion improved, the reaction time would increase since a better dispersion method would provide a greater reacting surface of phosphorus pentoxide - the equivalent of a greater amount.

Although the experimental data indicate that what are considered to be better dispersion methods produce lower reaction times, the explanation of this phenomenon is apparent. A tentative interpretation of this phenomenon is as follows: It is assumed that the phosphorus pentoxide reacts readily with a certain fraction of the asphalt to form "gritty particles". Possibly this fraction is that which tends to polymerize most readily. This assumption is justified by the

formation of numerous particles when the pentoxide is dispersed and by the appearance of a residue at the still bottom at the end of a pentoxide test. Hand stirring seems to produce more and larger particles than does mortar and pestle dispersion. It is also assumed that during blowing, the asphalt attacks and dissolves some of these gritty particles. The solution seems to take place only during the actual blowing since during the dispersion operation the gritty particles remain insoluble. It is believed that the gritty particles are a pentoxide-asphalt complex. Experimentally, it has been found that with a greater percent of phosphorus pentoxide, the time required to attain a given softening point was increased whereas with a better dispersion method the reaction time was decreased. A tentative explanation is that a larger percent of phosphorus pentoxide forms a larger amount of gritty particles and hence, during blowing, a longer time is required for the asphalt to completely dissolve these gritty particles. A better dispersion method forms smaller gritty particles with a larger total surface area for reaction and therefore a shorter time is required for their solution.

As illustrated in Figure 12 and Figure 23, the reaction rate varies only during the early stages of the blowing. In the later stages it reaches an almost constant value for all percentages of phosphorus pentoxide indicating the equivalent of a straight air blowing process. Thus it is believed that

during blowing the gritty particles are gradually settling out and hence reaction between the asphalt and the gritty particles occurs mostly in the early stages of the blowing. Possibly this accounts for the reduction in the ductility of pentoxide blown asphalts with softening points less than 130 °F. At the higher softening points obtainable by longer blowing, the gritty particles have either reacted with the asphalt or have settled out.

Effect of Dispersion Method on Penetration, Viscosity, Ductility, Softening Point Relationships

Further evidences of the importance of the dispersion method is indicated by the fact that the penetration-softening point, viscosity-softening point, and ductility-softening point relationships are changed appreciably from those produced by the straight blown test. Figures 24 to 27 inclusive show the effect of the dispersion method on the penetration-softening point relationship. It is seen that dispersion by mortar and pestle or mortar, pestle and screen give almost identical results. These two methods produce the best penetration increase for a given softening point, and possibly this is the maximum effect that can be obtained with 1.0 percent phosphorus pentoxide. Dispersion of the pentoxide by hand stirring and by use of carbon tetrachloride produce an intermediate effect on the penetration-softening point relationship. In commercial operations, dispersion by mortar and pestle would not be practical. It is believed,

however, that in commercial operations the same degree of dispersion could be obtained in a ball mill.

The effect of the dispersion method on the viscosity-softening point relationship is shown in Figure 28. As with the penetrations, dispersion by mortar and pestle or mortar, pestle and screen produce maximum viscosity increases for a given softening point.

The results of the ductility test are illustrated in Figure 29. The same general type of ductility-softening point relationship as observed earlier is again obtained. Generally speaking, pentoxide blown asphalts with softening points of approximately 130°F. or lower show a much lower ductility than the straight blown asphalt. For higher softening point asphalts there seems to be no appreciable differences in the ductilities.

Effect of Straight and "Catalytic" Air Blowing on Specific Gravity and Solubility in Carbon Tetrachloride

For every pilot test, at least 4 samples with different softening points were tested for their specific gravity at 77 °F. and their solubility in carbon tetrachloride. As illustrated in Figure 30, as the softening point of the blown asphalt increases from 107 °F. to 235 °F., the specific gravity changes from approximately 1.004 to about 1.026. There seems to be no appreciable difference in the measured specific gravity between the straight blown and pentoxide blown asphalts.

With the presence of a large residue in the still at

the end of the pentoxide tests, it was expected that the solubility of the pentoxide blown samples would be reduced markedly, especially when samples were all drawn from the lowest sampling connection flush with the still bottom. However, in all the samples the solubility was found to be greater than 99 percent. As indicated in Figure 31, on the average the straight blown samples show a solubility of 99.8 percent and the pentoxide blown samples a solubility of 99.6 percent, a difference of only 0.2 percent. This is believed barely significant.

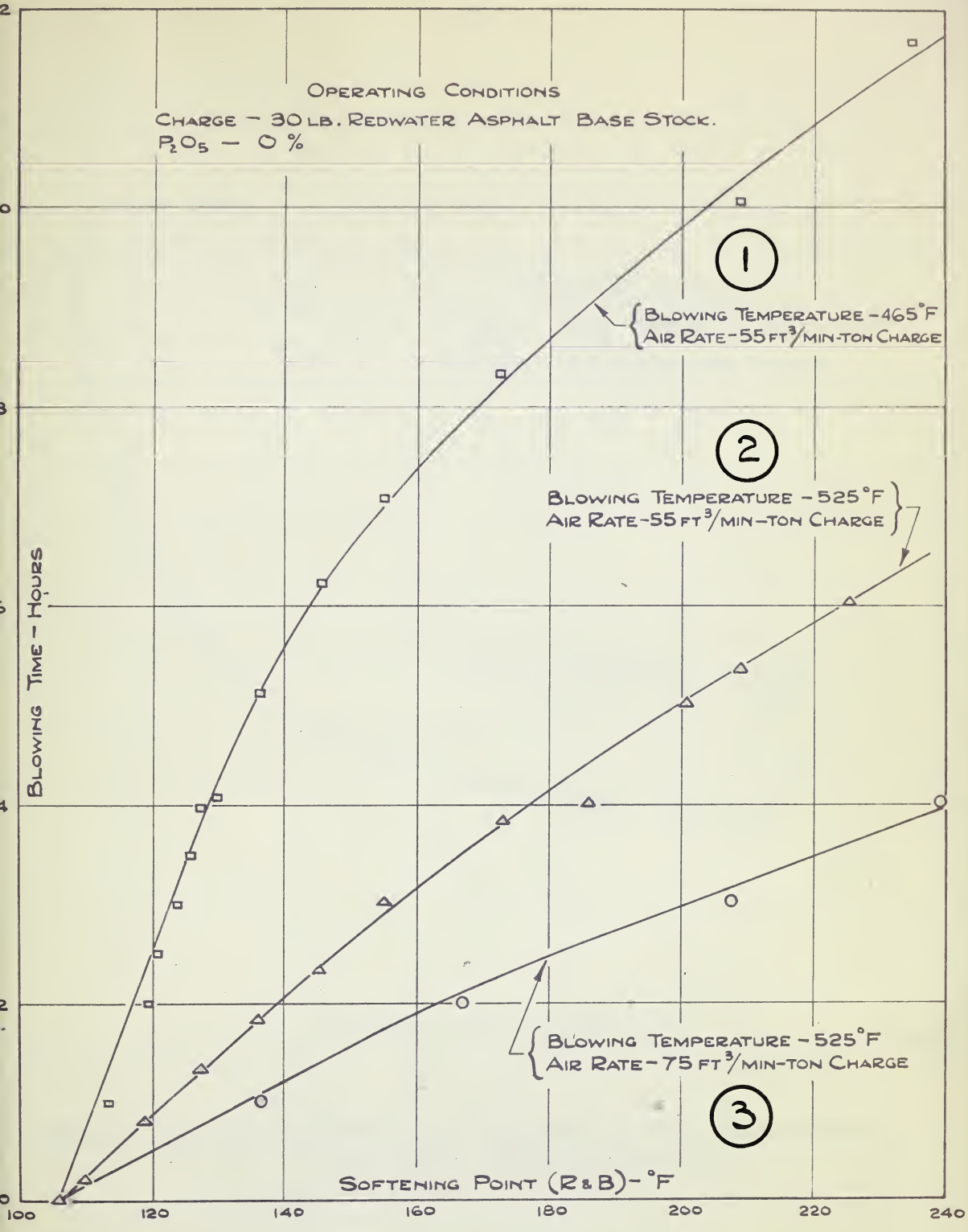

FIG. 5. EFFECT OF BLOWING TEMPERATURE & AIR RATE ON REACTION TIME.

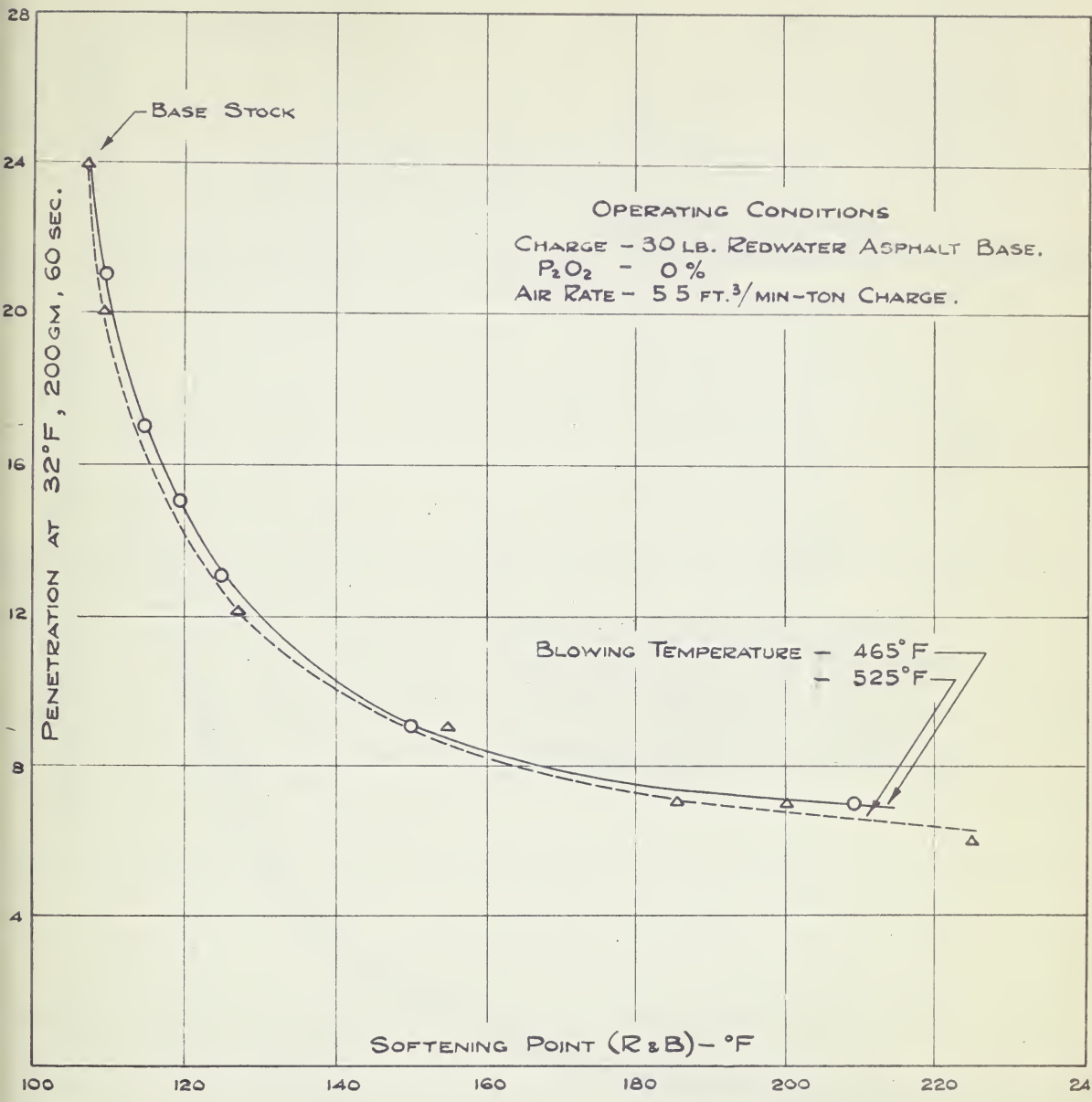

FIG.6. EFFECT OF BLOWING TEMPERATURE ON PENETRATION AT 32°F, 200 GM, 60 SEC.

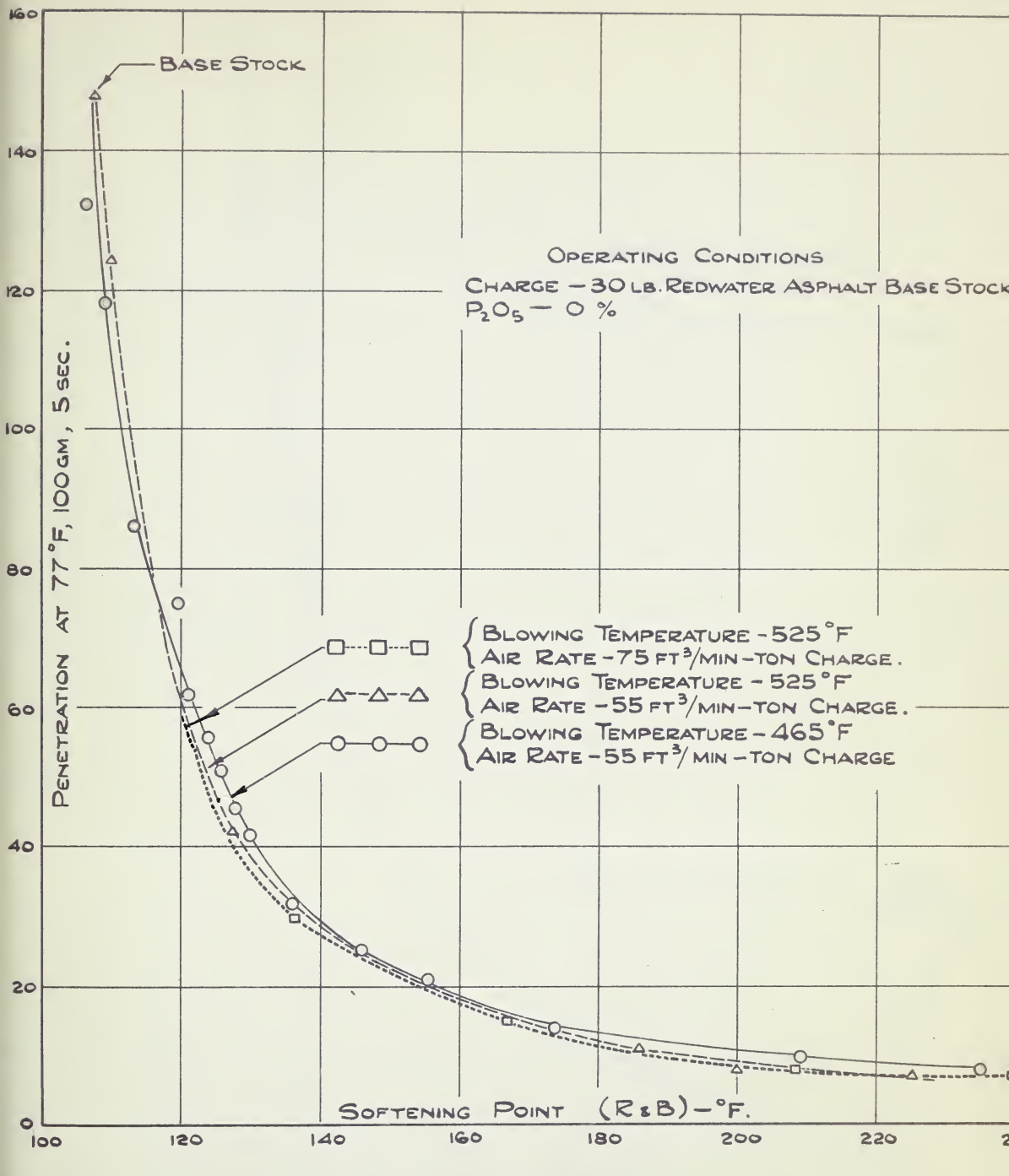

FIG. 7. EFFECT OF BLOWING TEMPERATURE AND AIR RATE ON PENETRATION AT 77 °F, 100 GM, 5 SEC.

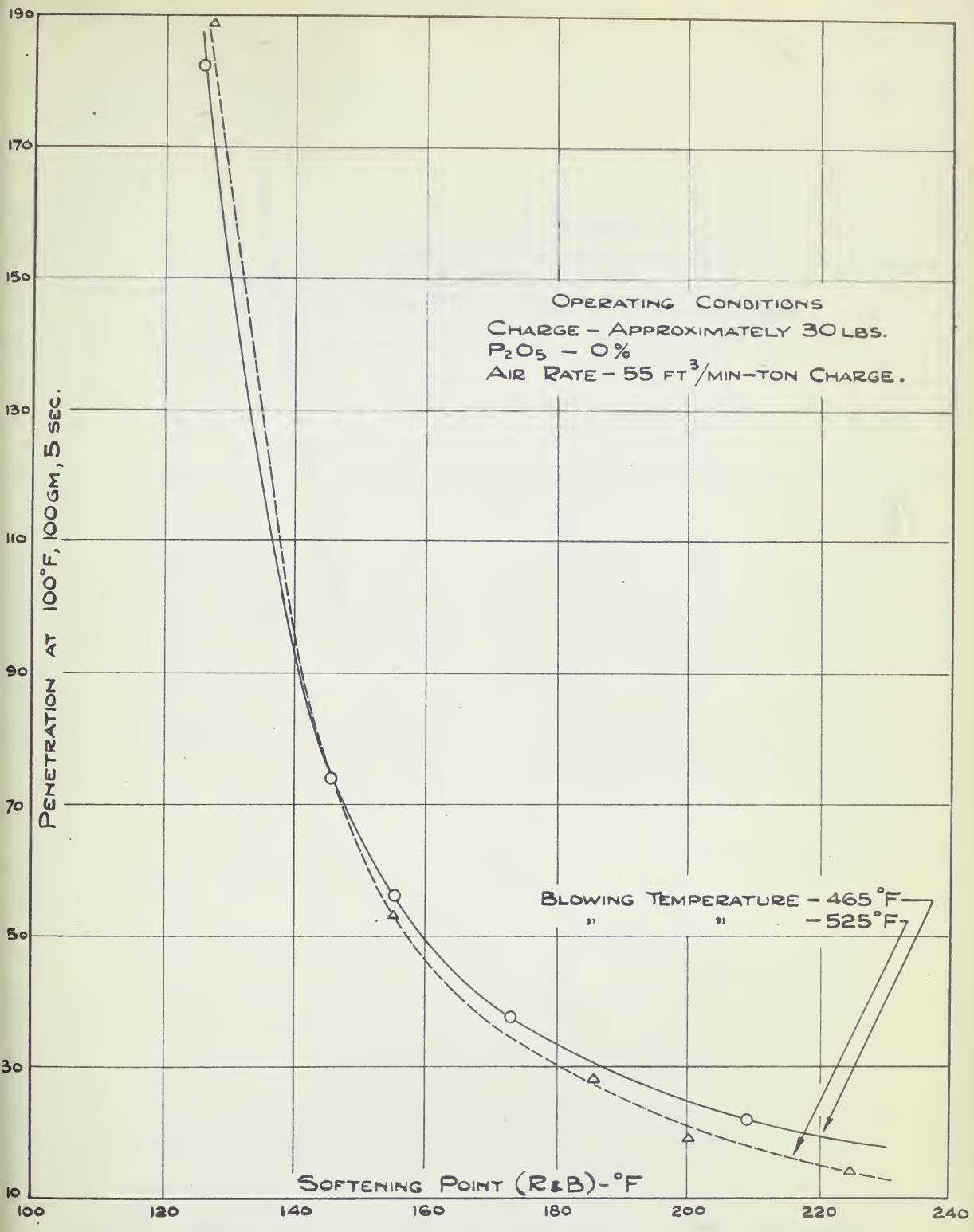

FIG.8. EFFECT OF BLOWING TEMPERATURE ON PENETRATION AT 100°F, 100 GM, 5 SEC.

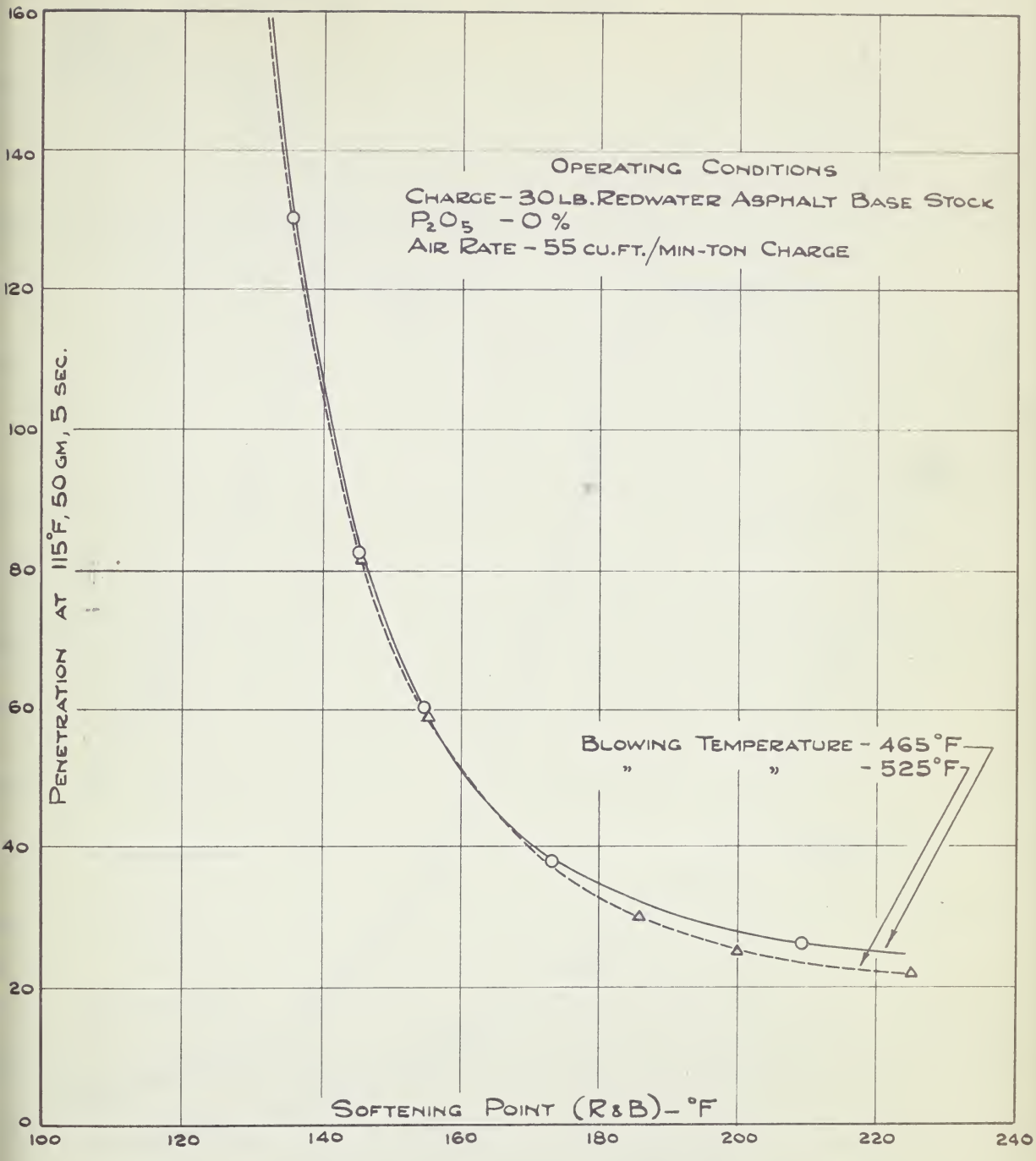

FIG. 9. EFFECT OF BLOWING TEMPERATURE ON PENETRATION AT 115°F, 50 GM, 5 SEC.

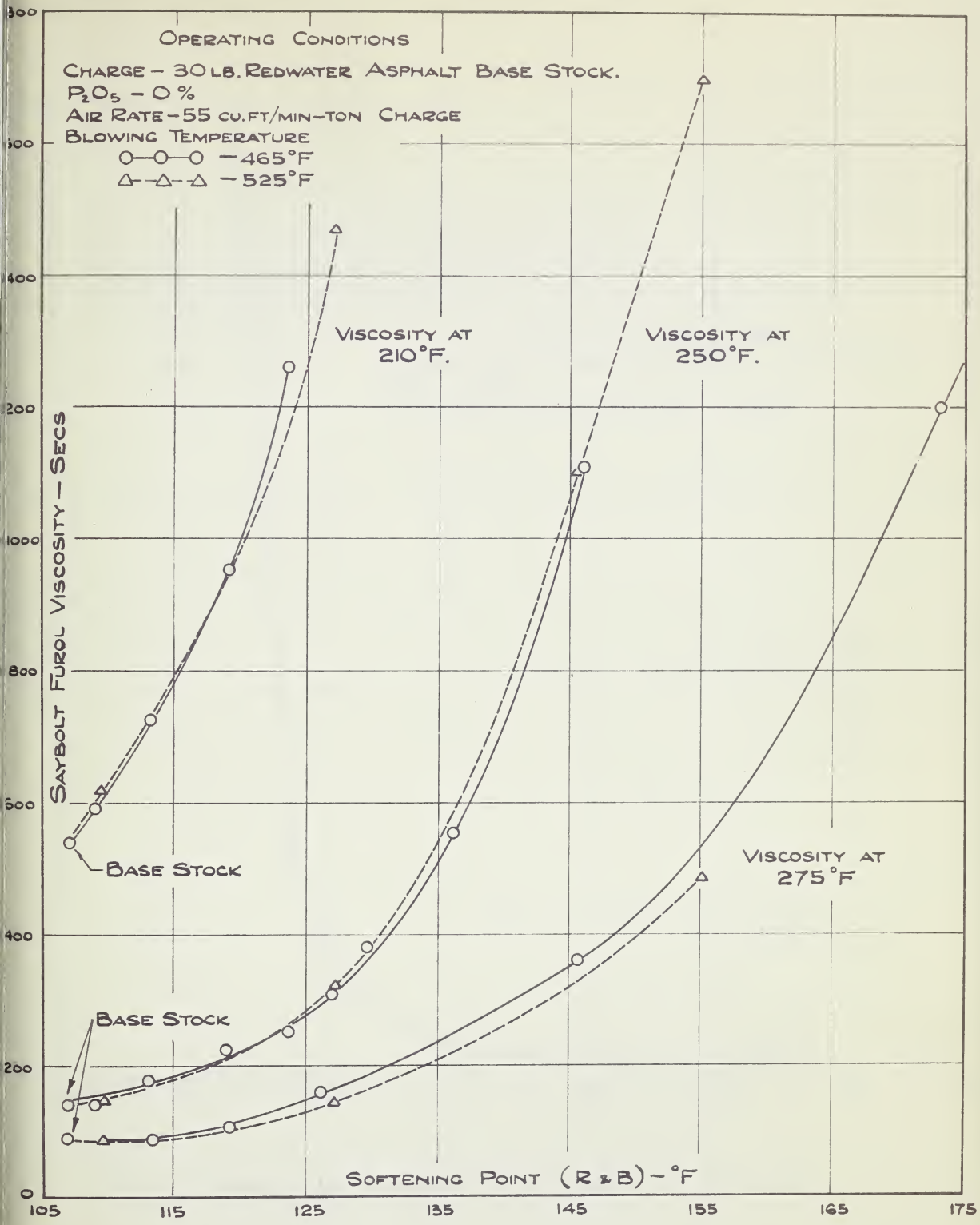

FIG. 10. EFFECT OF BLOWING TEMPERATURE SAYBOLT FUROL VISCOSITY.

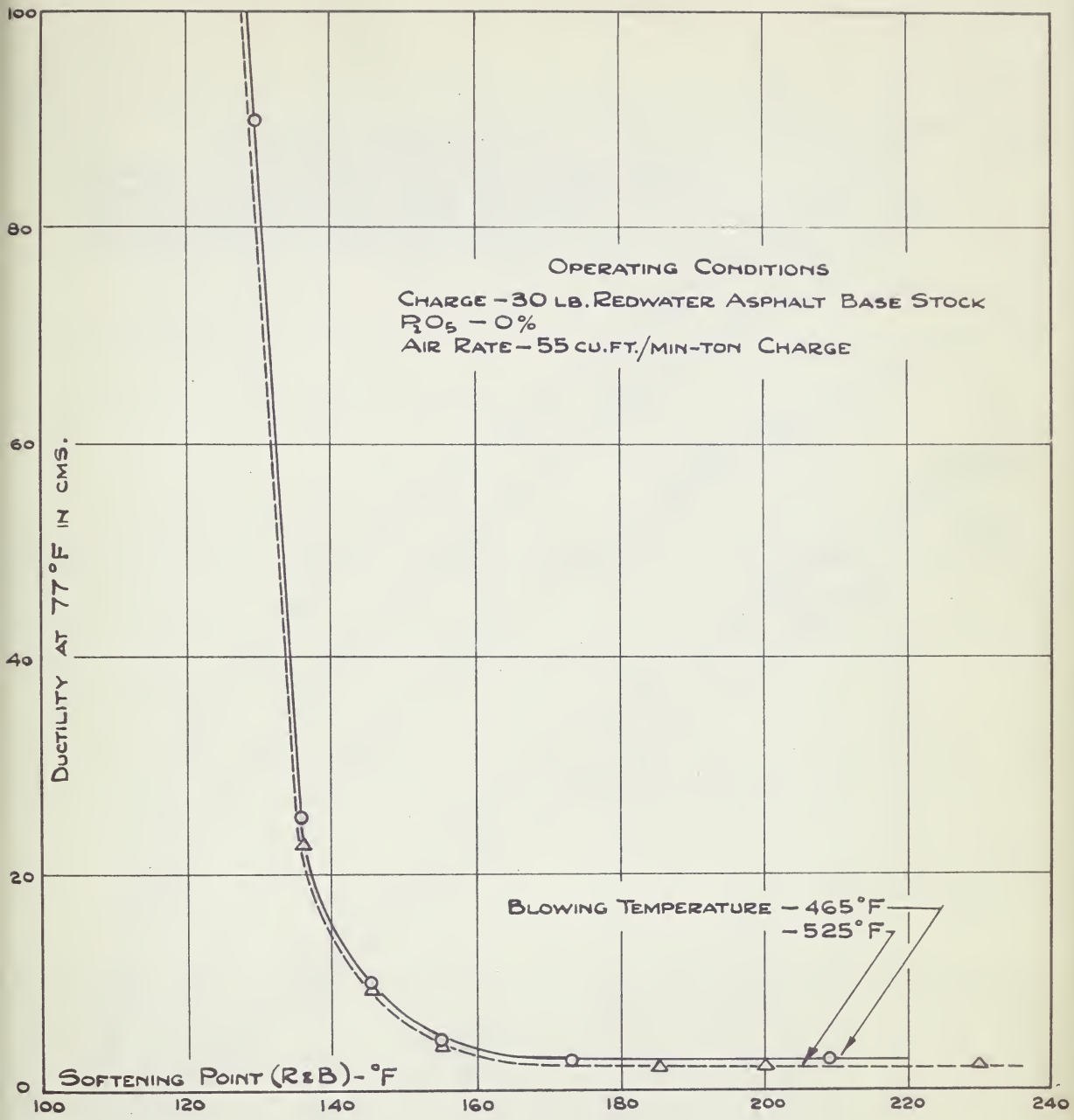

FIG. 11. EFFECT OF BLOWING TEMPERATURE ON DUCTILITY.

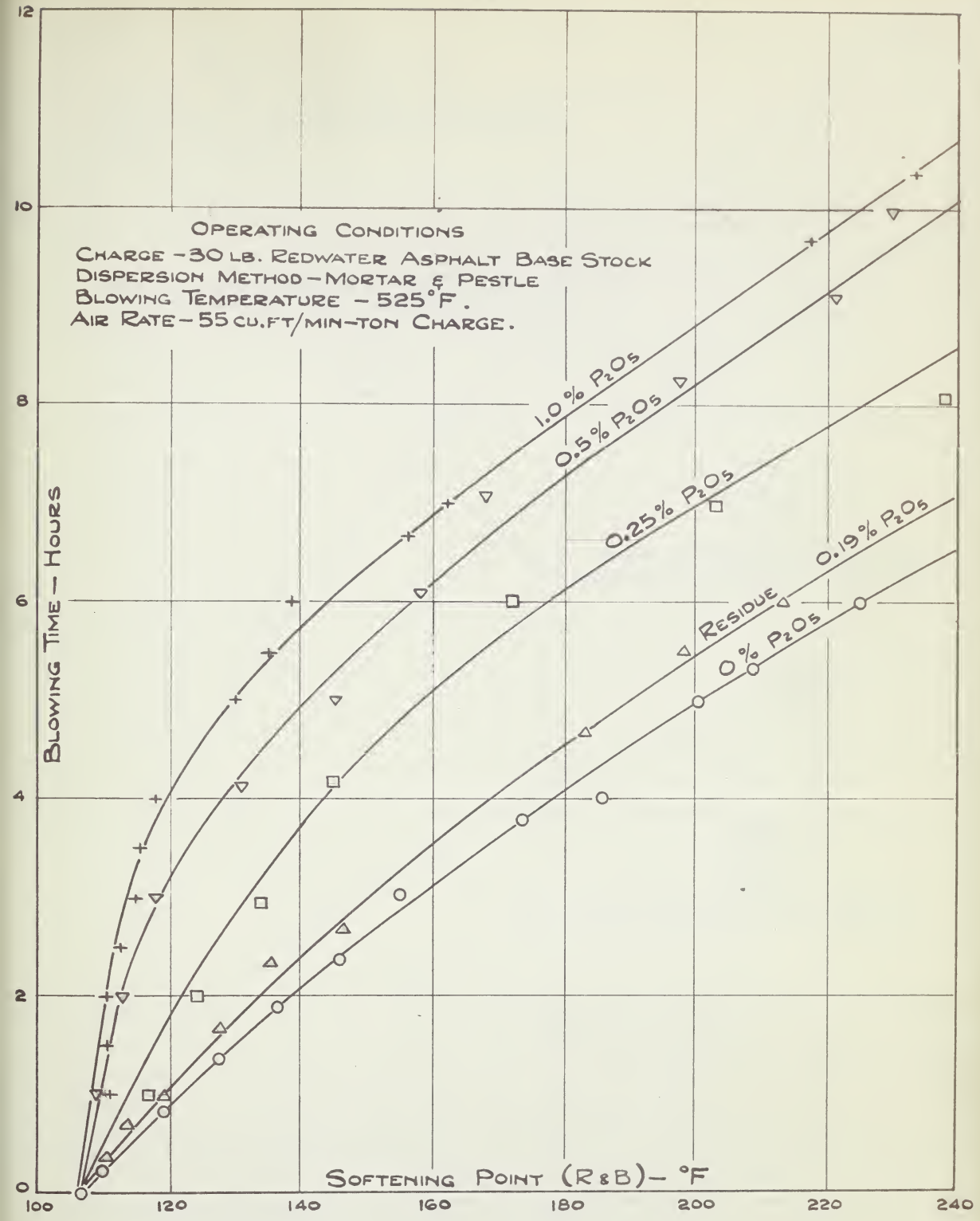

FIG. 12. EFFECT OF PHOSPHORUS PENTOXIDE ON REACTION TIME.

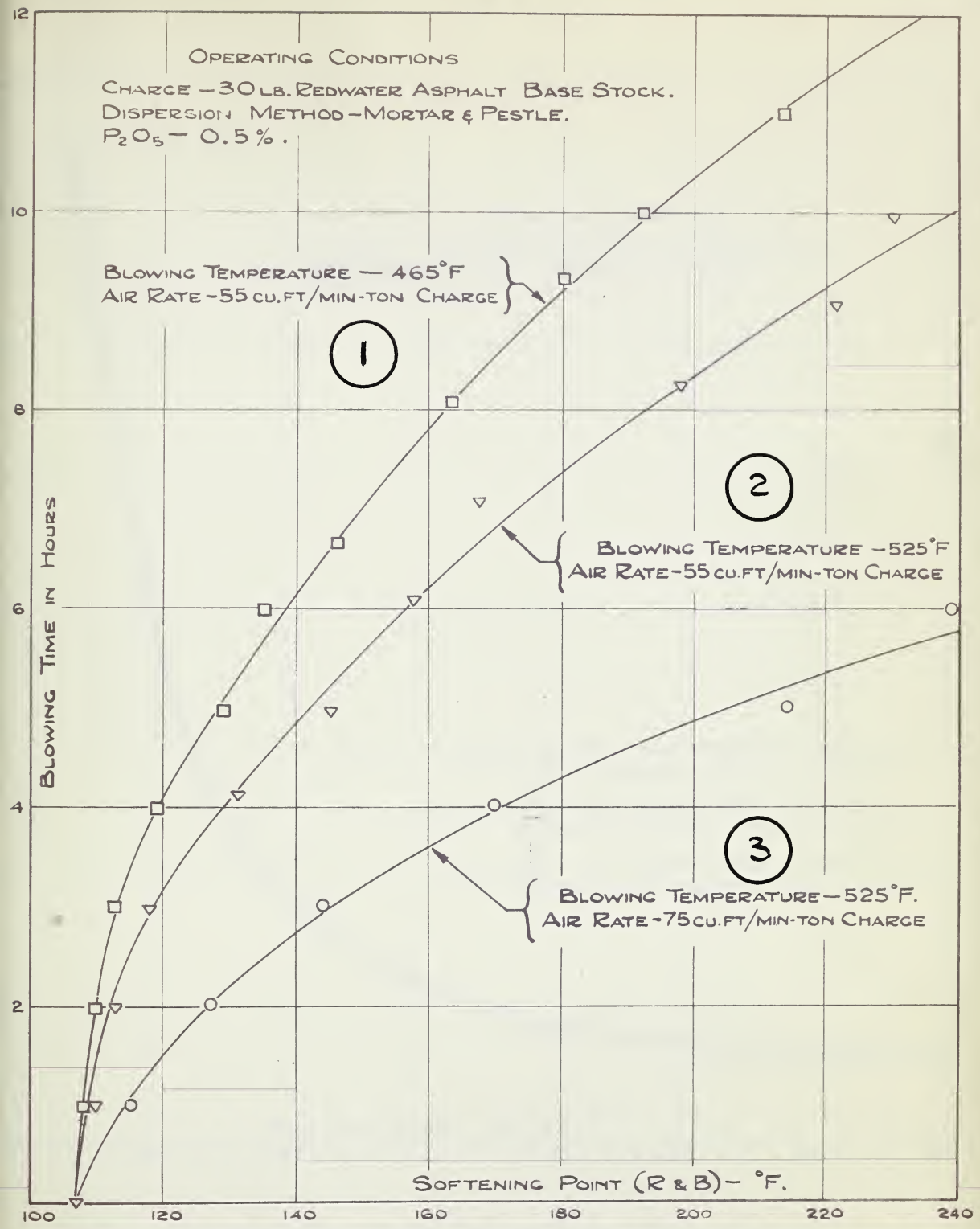

Fig. 13. Effect of Blowing Temperature & Air Rate on Reaction Time.

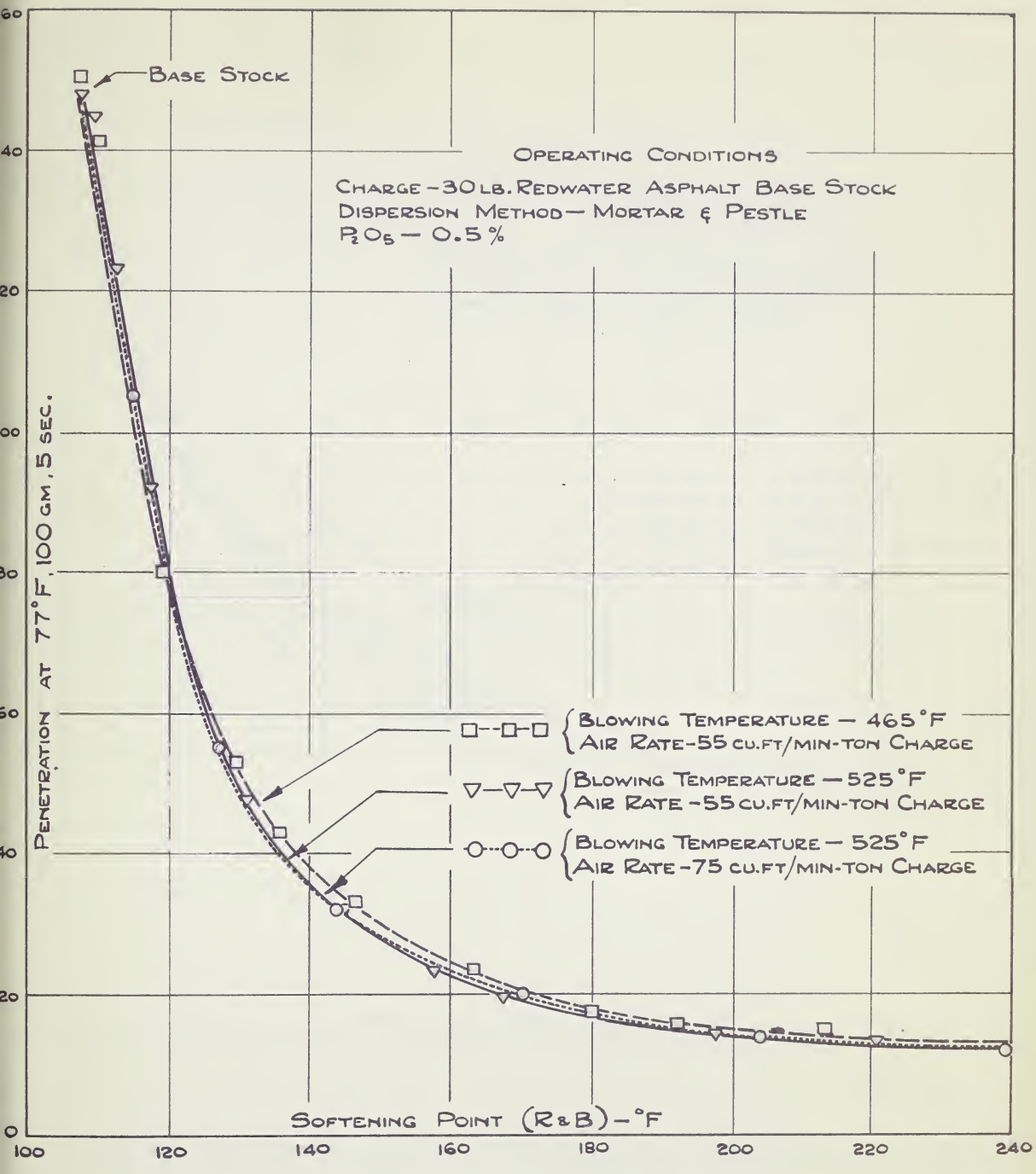

Fig. 14. Effect of Blowing Temperature & Air Rate on Penetration at 77°F, 100 gm, 5 sec.

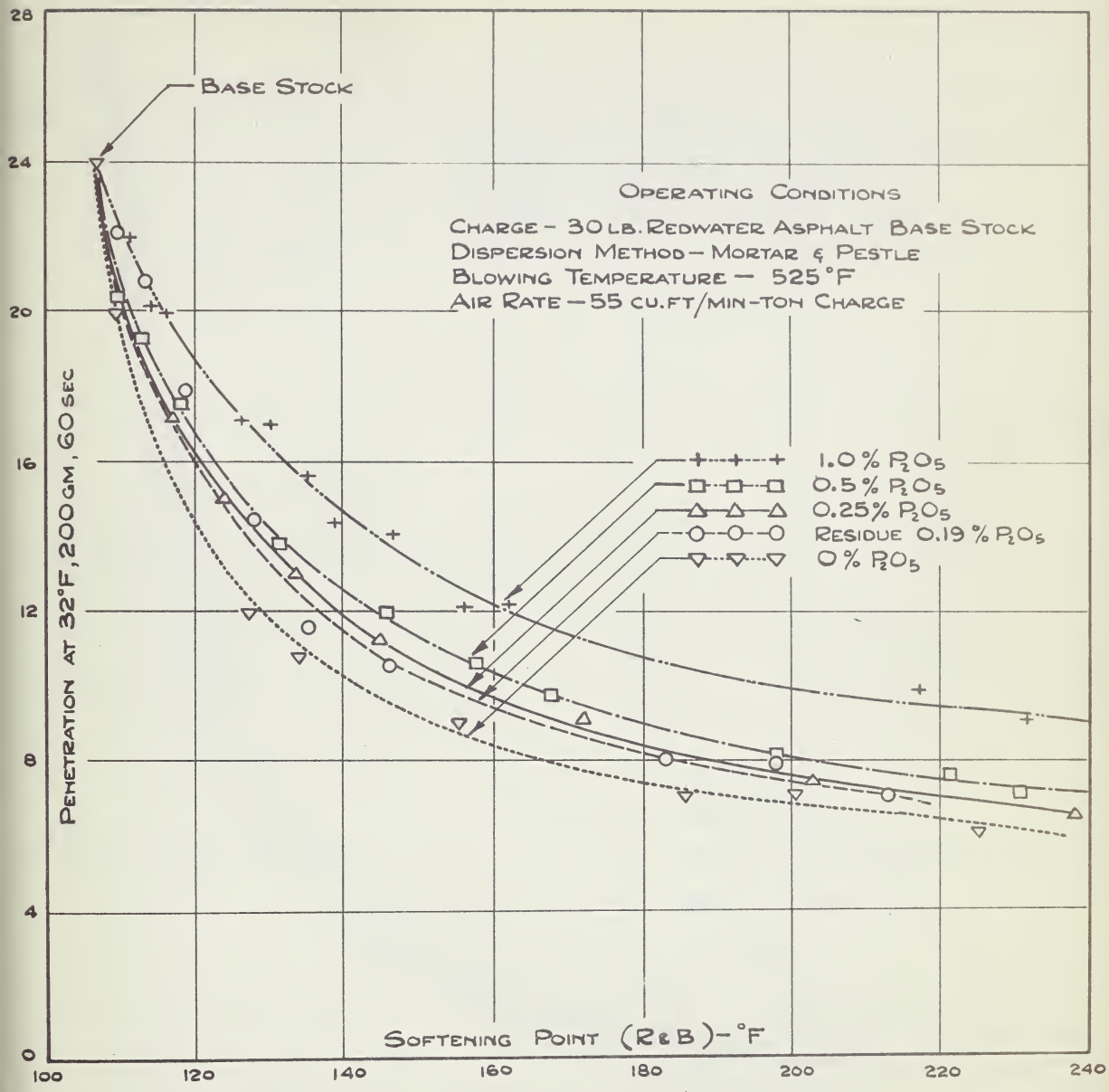

FIG.15. EFFECT OF PHOSPHORUS PENTOXIDE ON PENETRATION AT 32 °F.

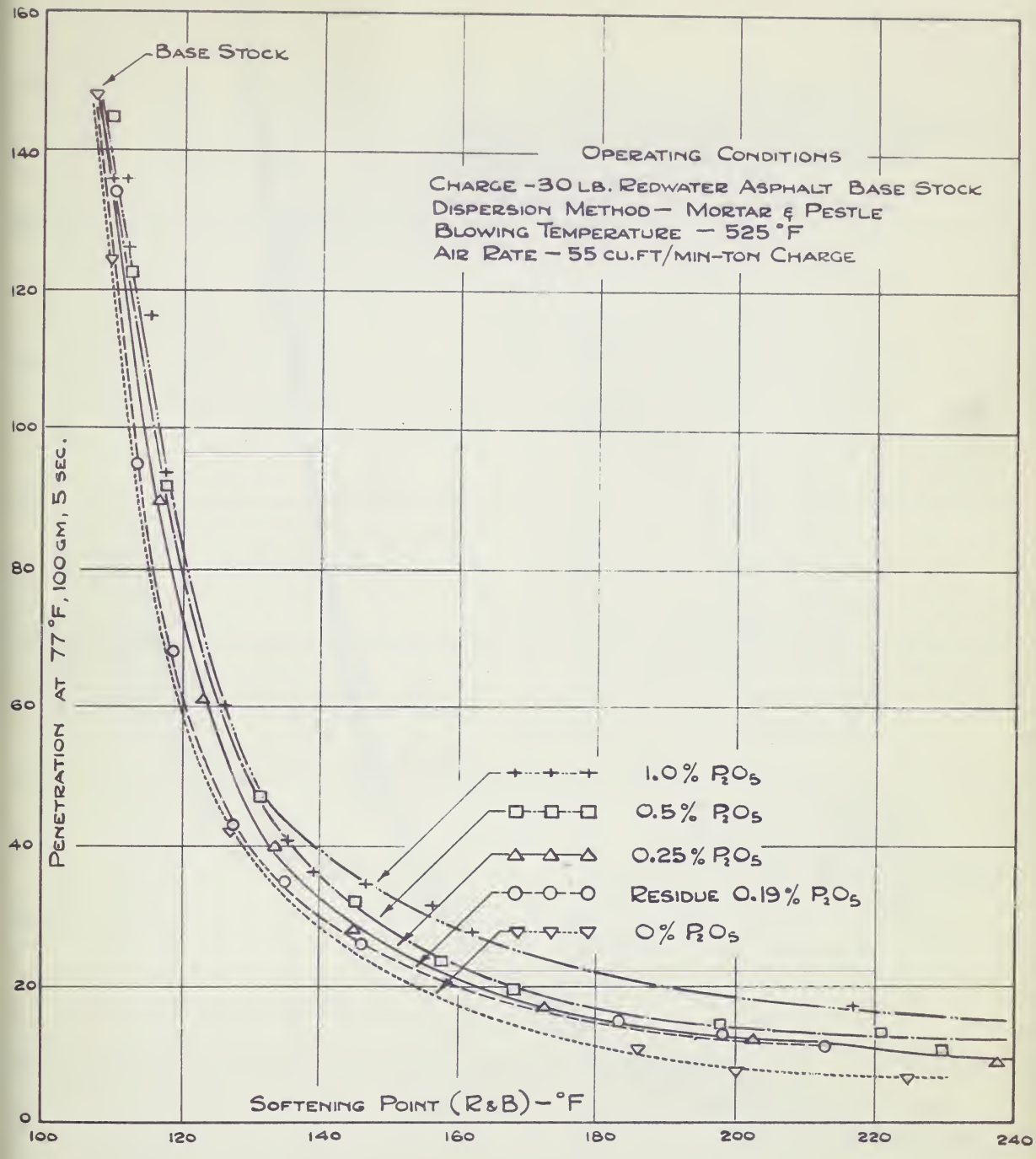

FIG. 16. EFFECT OF PHOSPHORUS PENTOXIDE ON PENETRATION AT 77 °F.

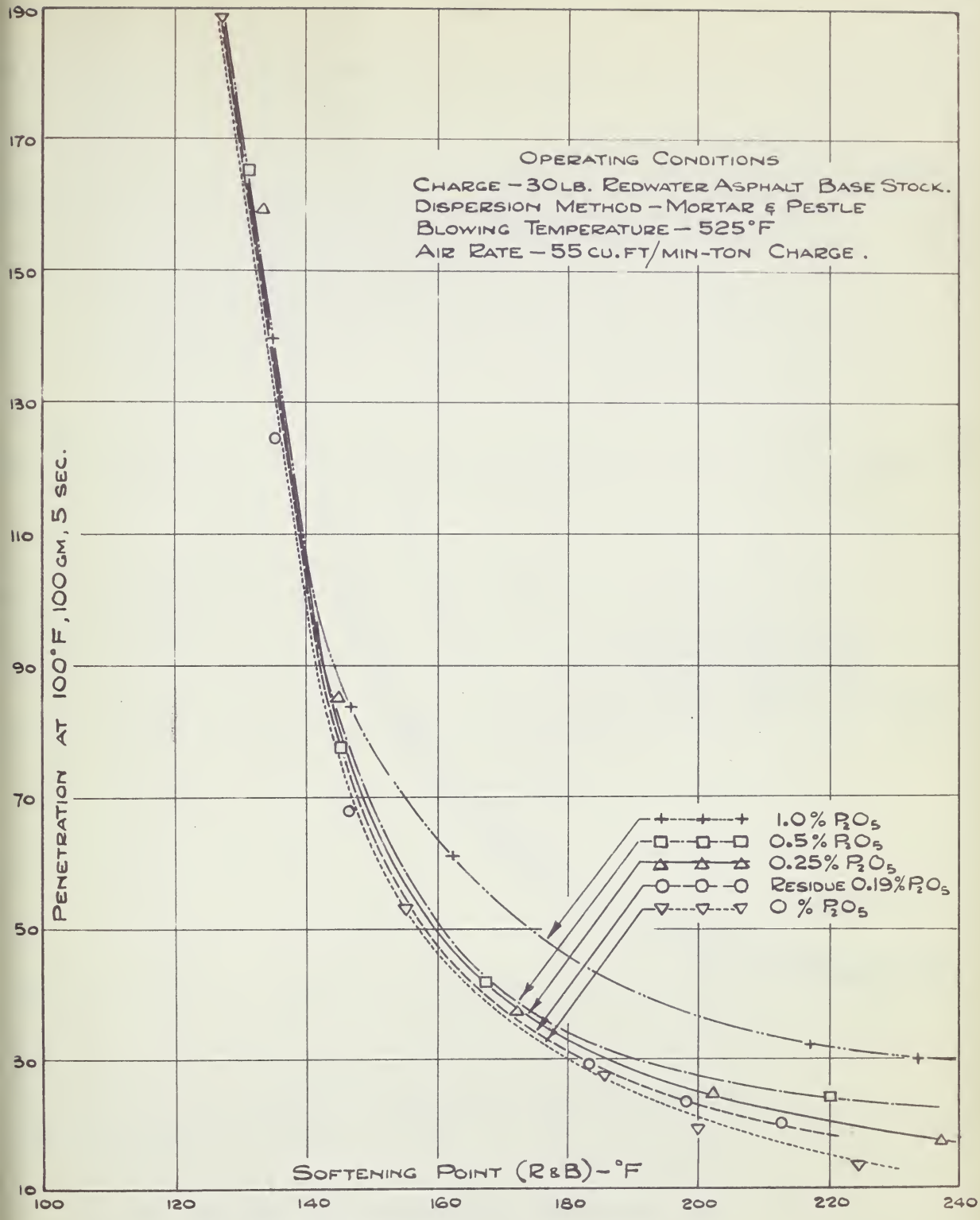

FIG. 17. EFFECT OF PHOSPHORUS PENTOXIDE ON PENETRATION AT 100°F.

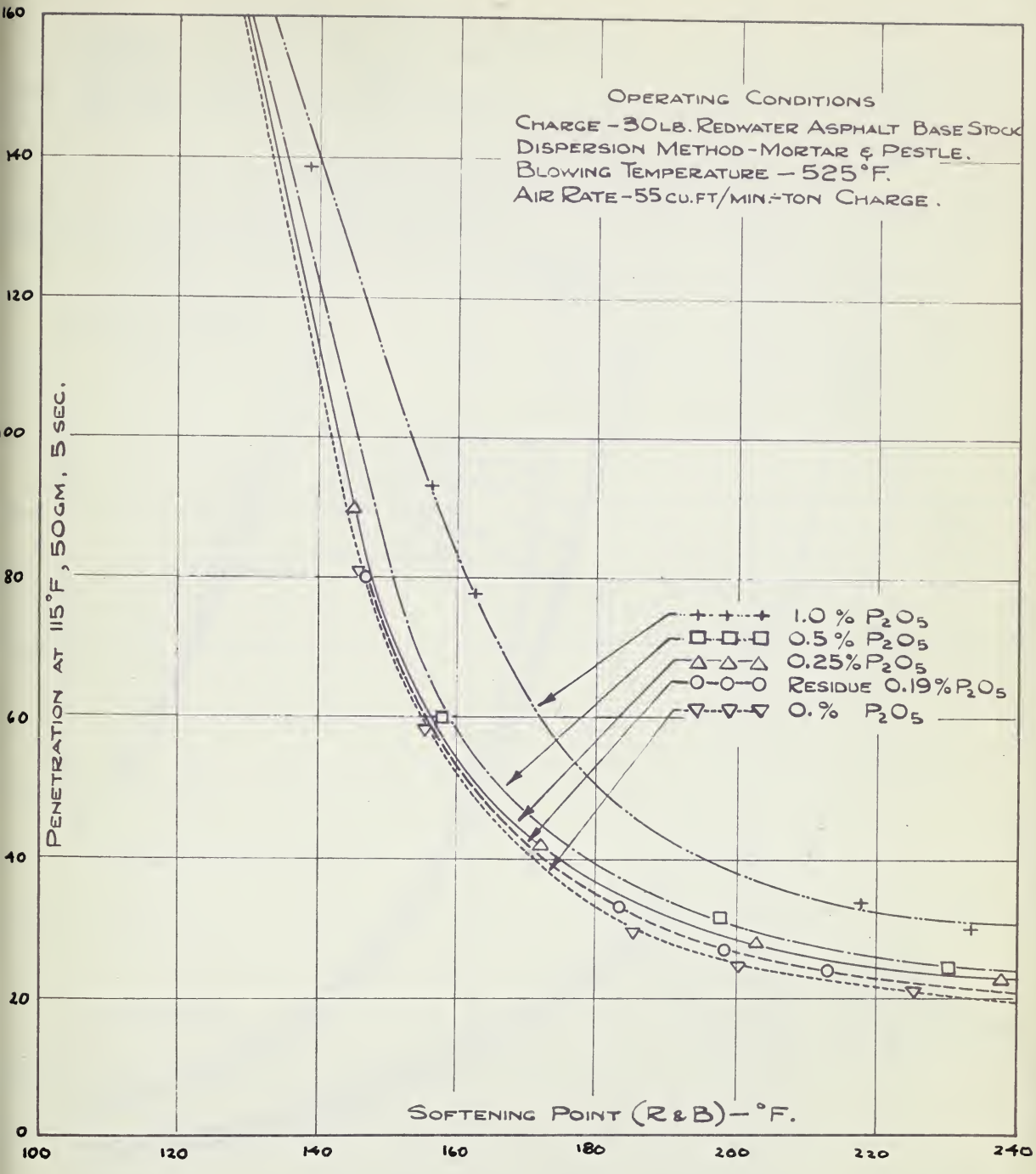

FIG. 18. EFFECT OF PHOSPHORUS PENTOXIDE ON PENETRATION AT 115°F.

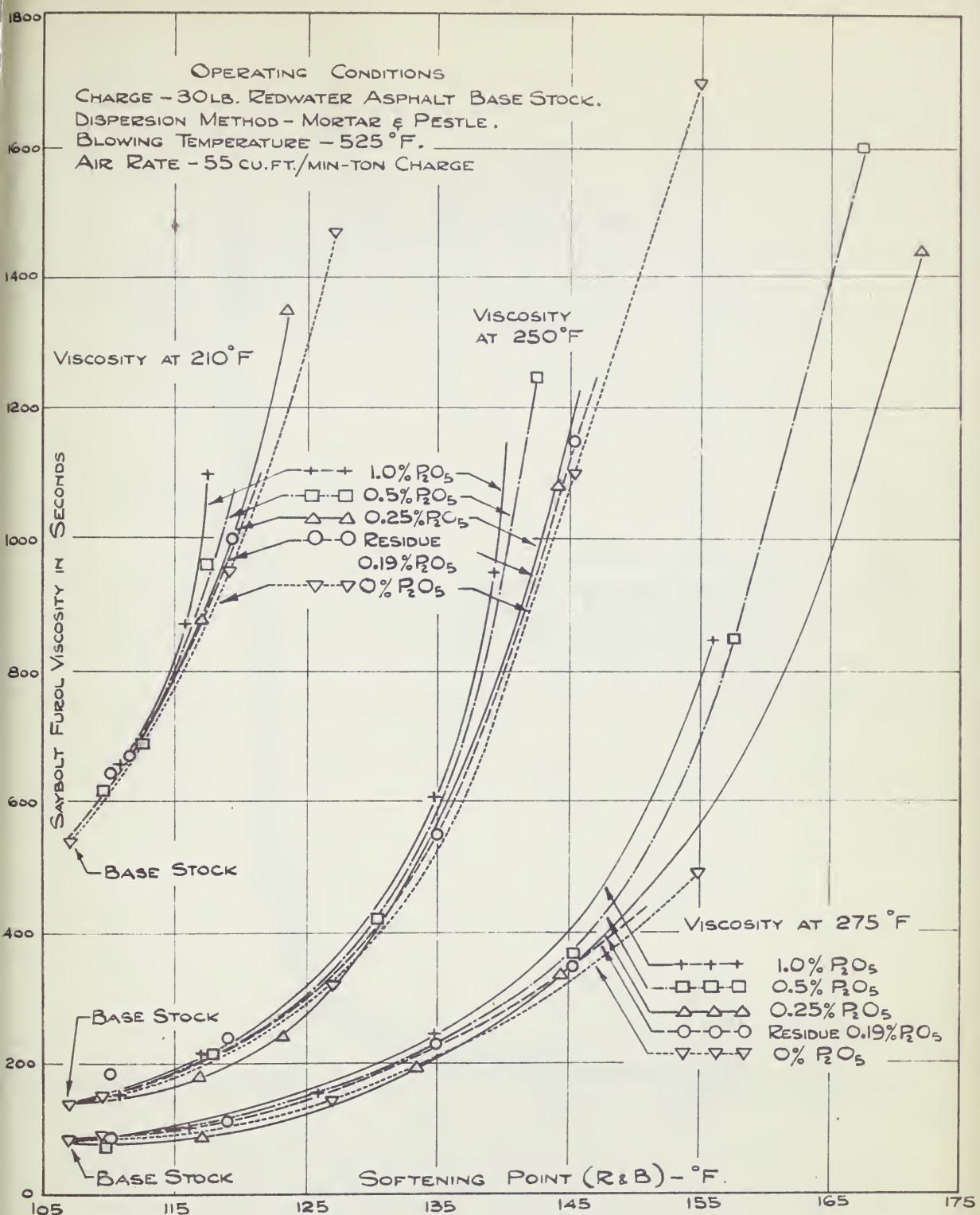

FIG. 19. EFFECT OF PHOSPHORUS PENTOXIDE ON SAYBOLT-FUROL VISCOSITY

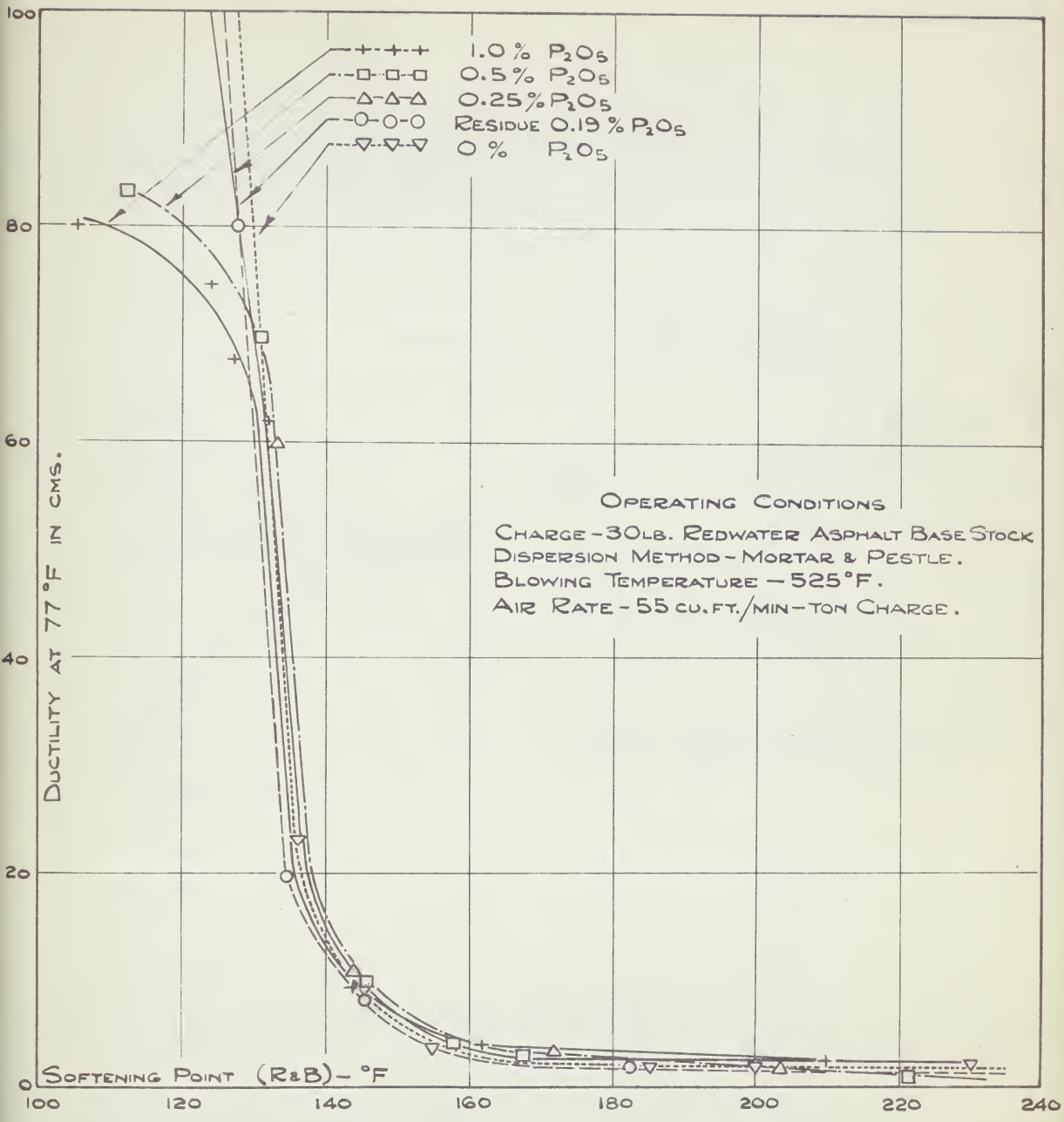

Fig. 20. Effect of Phosphorus Pentoxide on Ductility.

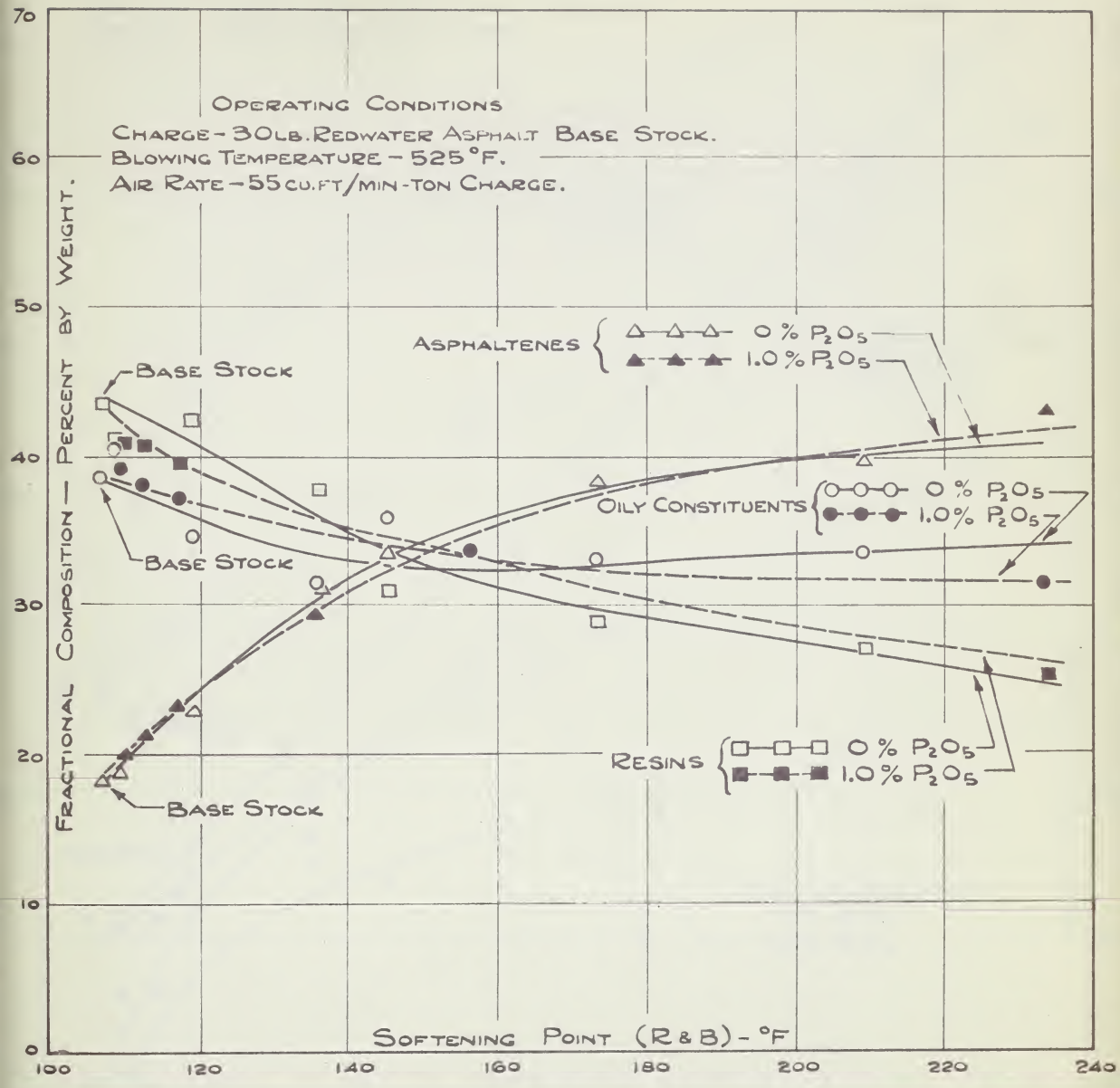

Fig. 21. Effect of Phosphorus Pentoxide on the Fractional Composition.

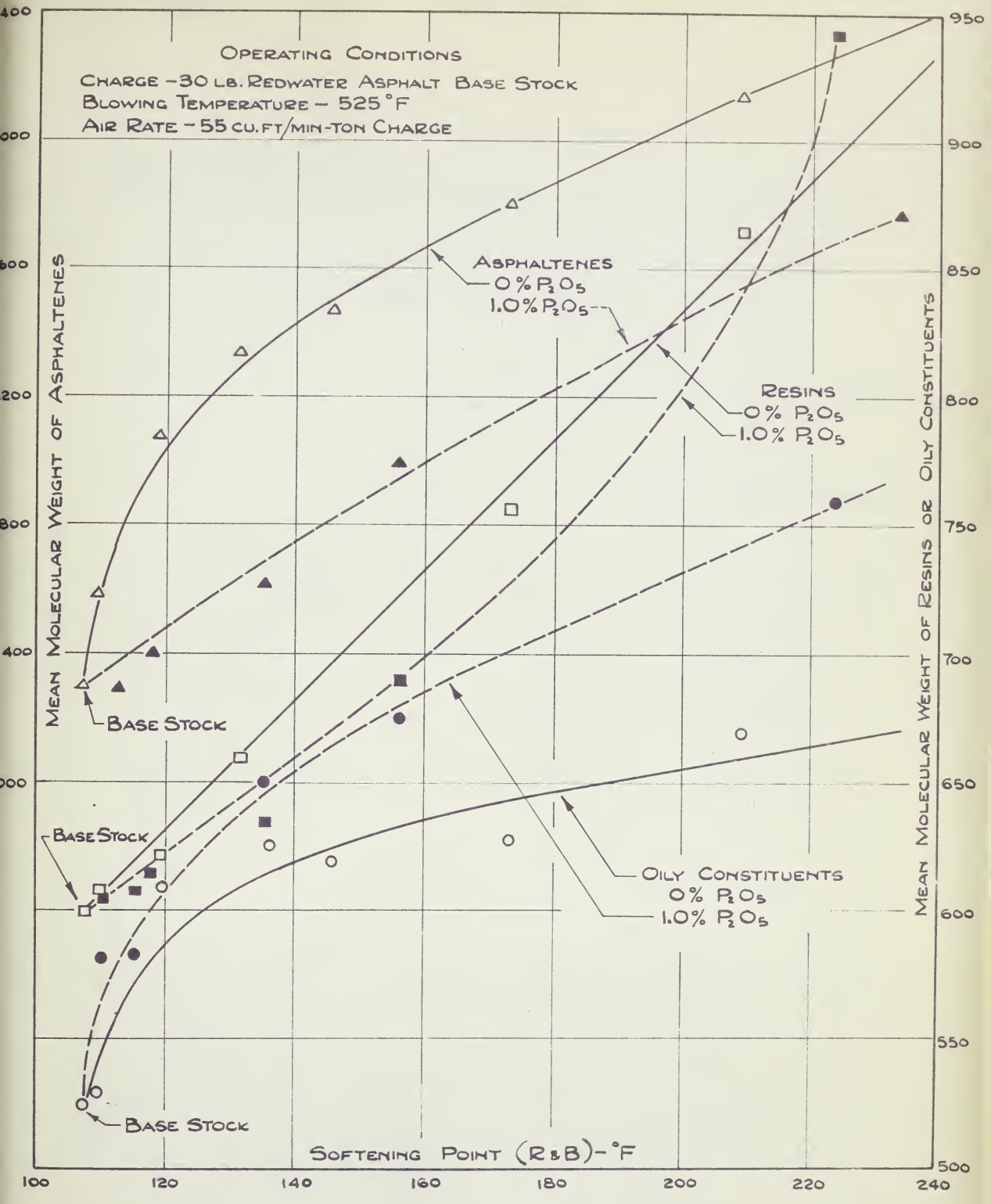

FIG.22. EFFECT OF PHOSPHORUS PENTOXIDE ON THE MEAN MOLECULAR WEIGHT OF ASPHALTENES, RESINS & OILY CONSTITUENTS.

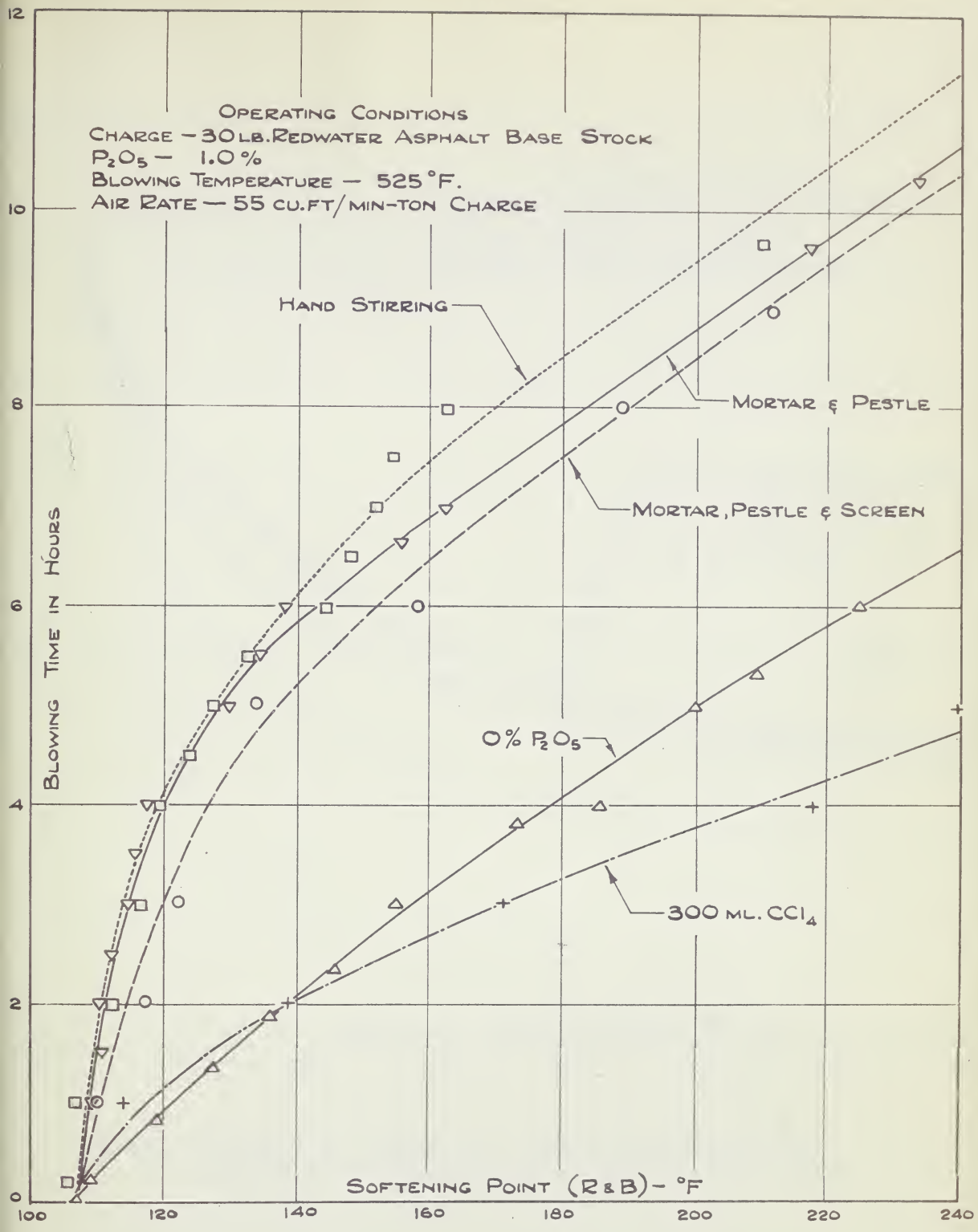

FIG. 23. EFFECT OF DISPERSION METHOD FOR PHOSPHORUS PENTOXIDE ON REACTION TIME.

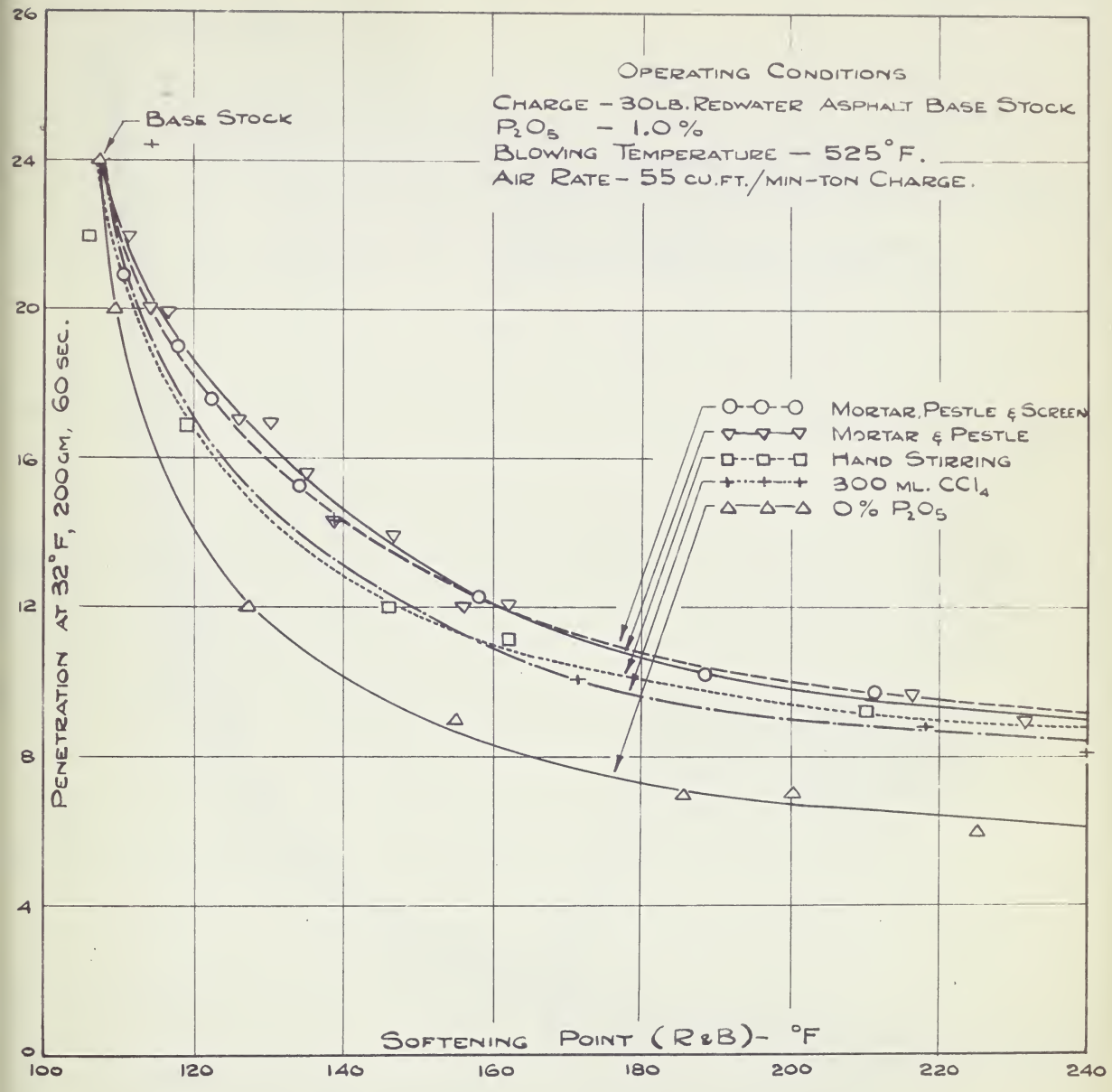

FIG. 24. EFFECT OF DISPERSION METHOD FOR PHOSPHORUS PENTOXIDE ON PENETRATION AT 32°F, 200 GM, 60 SEC.

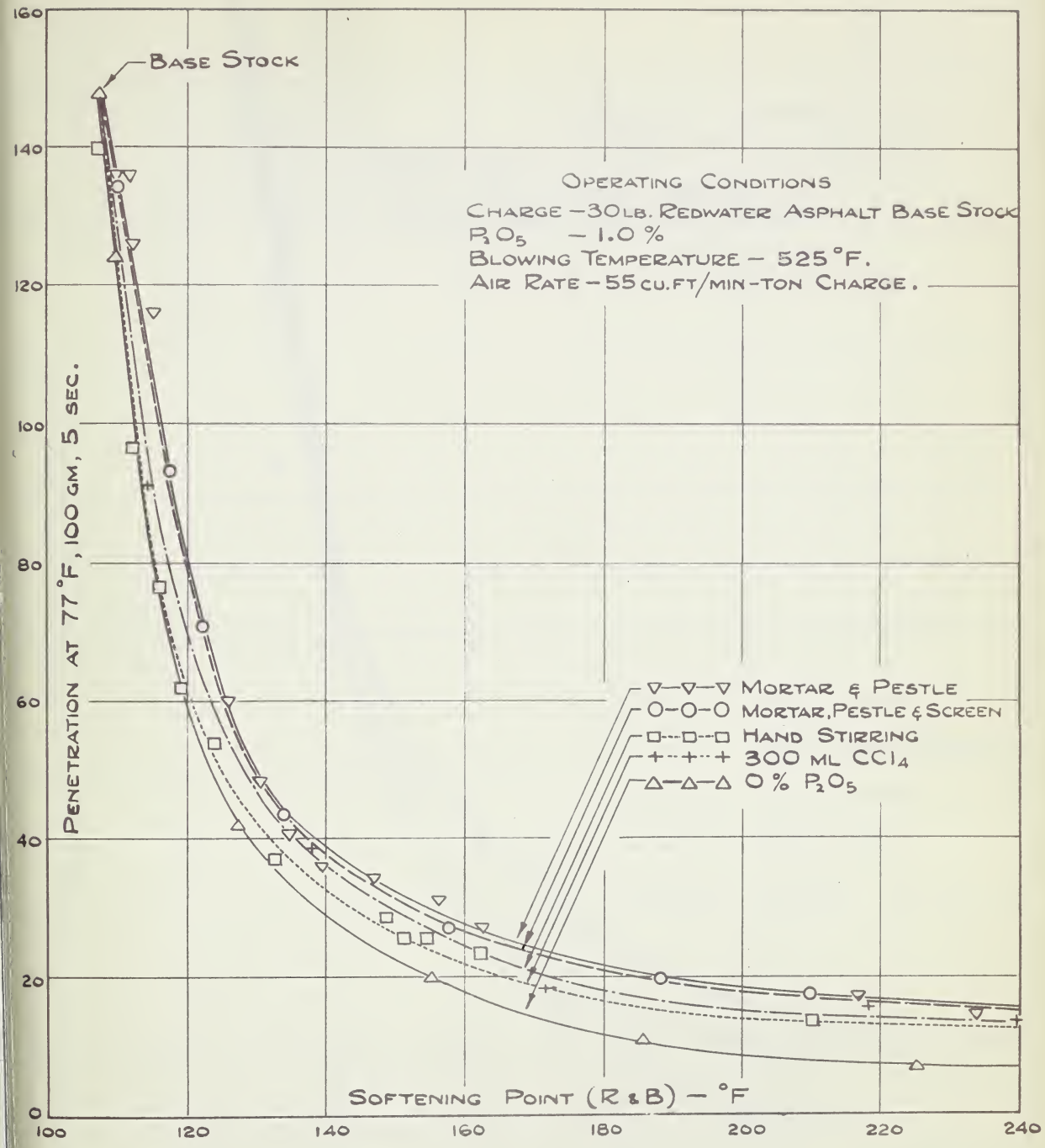

FIG. 25. EFFECT OF DISPERSION METHOD FOR PHOSPHORUS PENTOXIDE ON PENETRATION AT 77 °F, 100 GM, 5 SEC.

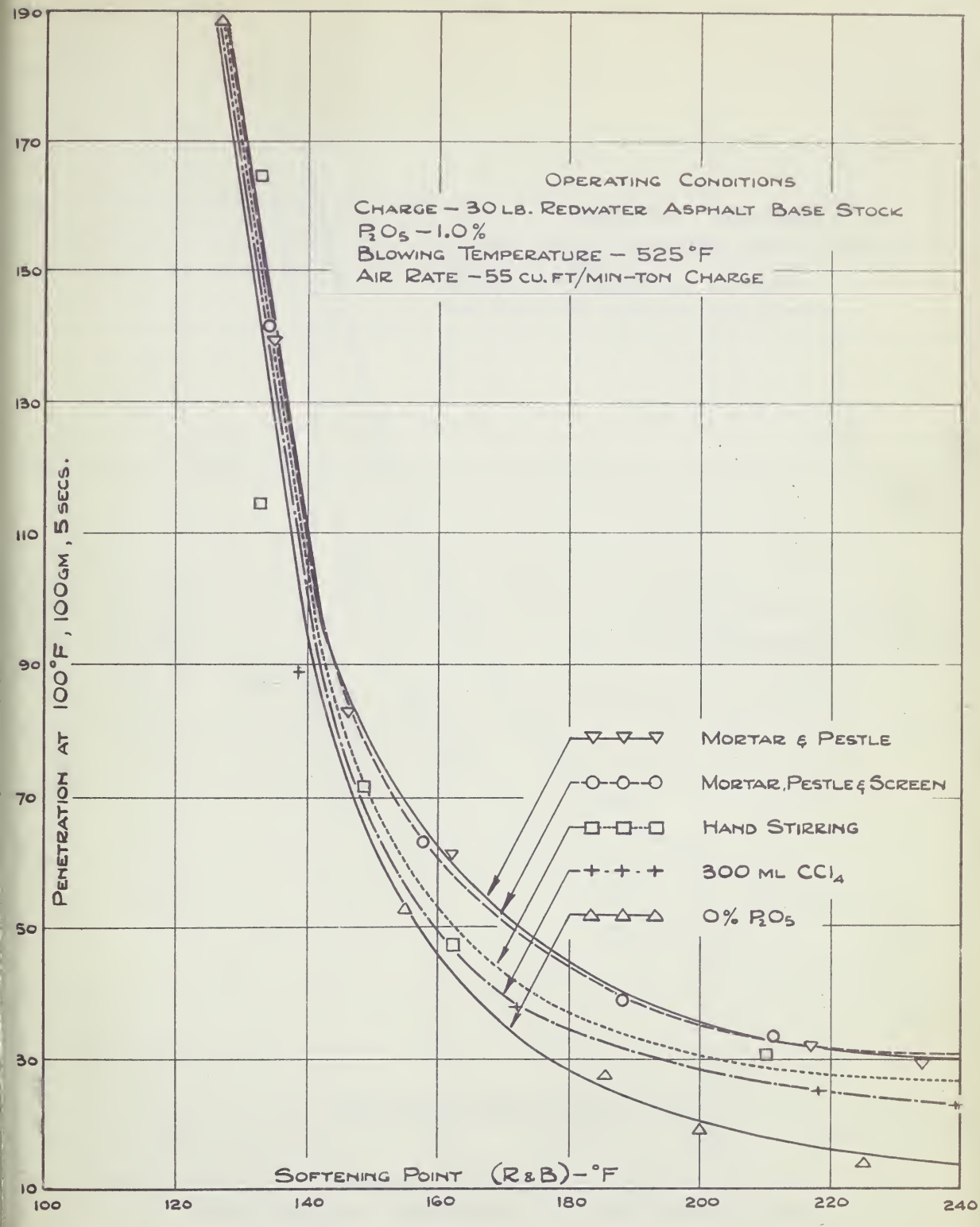

FIG. 26. EFFECT OF DISPERSION METHOD FOR PHOSPHORUS PENTOXIDE ON PENETRATION AT 100°F, 100 GM, 5 SEC.

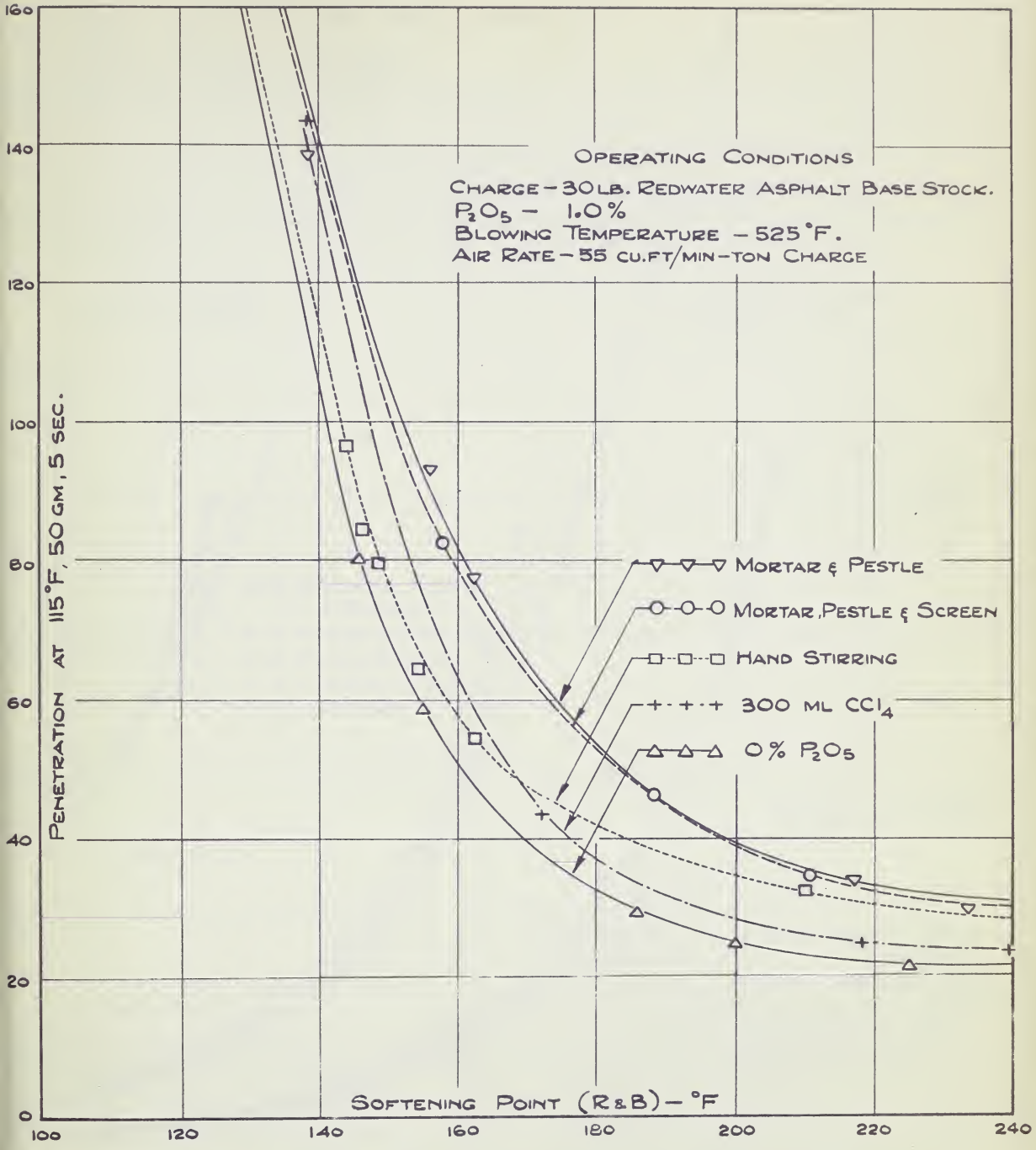

FIG. 27. EFFECT OF DISPERSION METHOD FOR PHOSPHORUS PENTOXIDE ON PENETRATION AT 115°F, 50GM, 5 SEC.

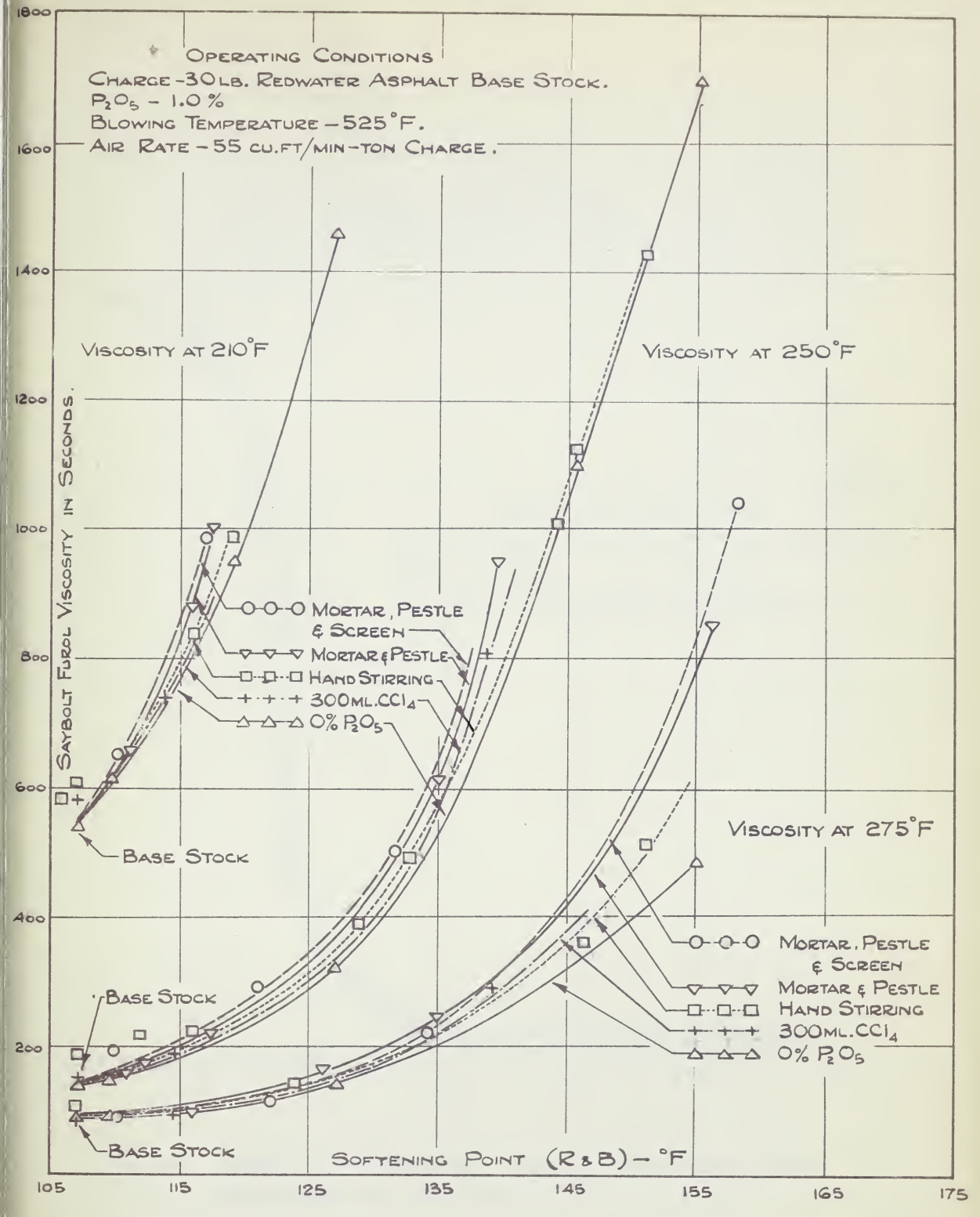

Fig. 28. Effect of Dispersion Method for Phosphorus Pentoxide on Saybolt Furol Viscosity.

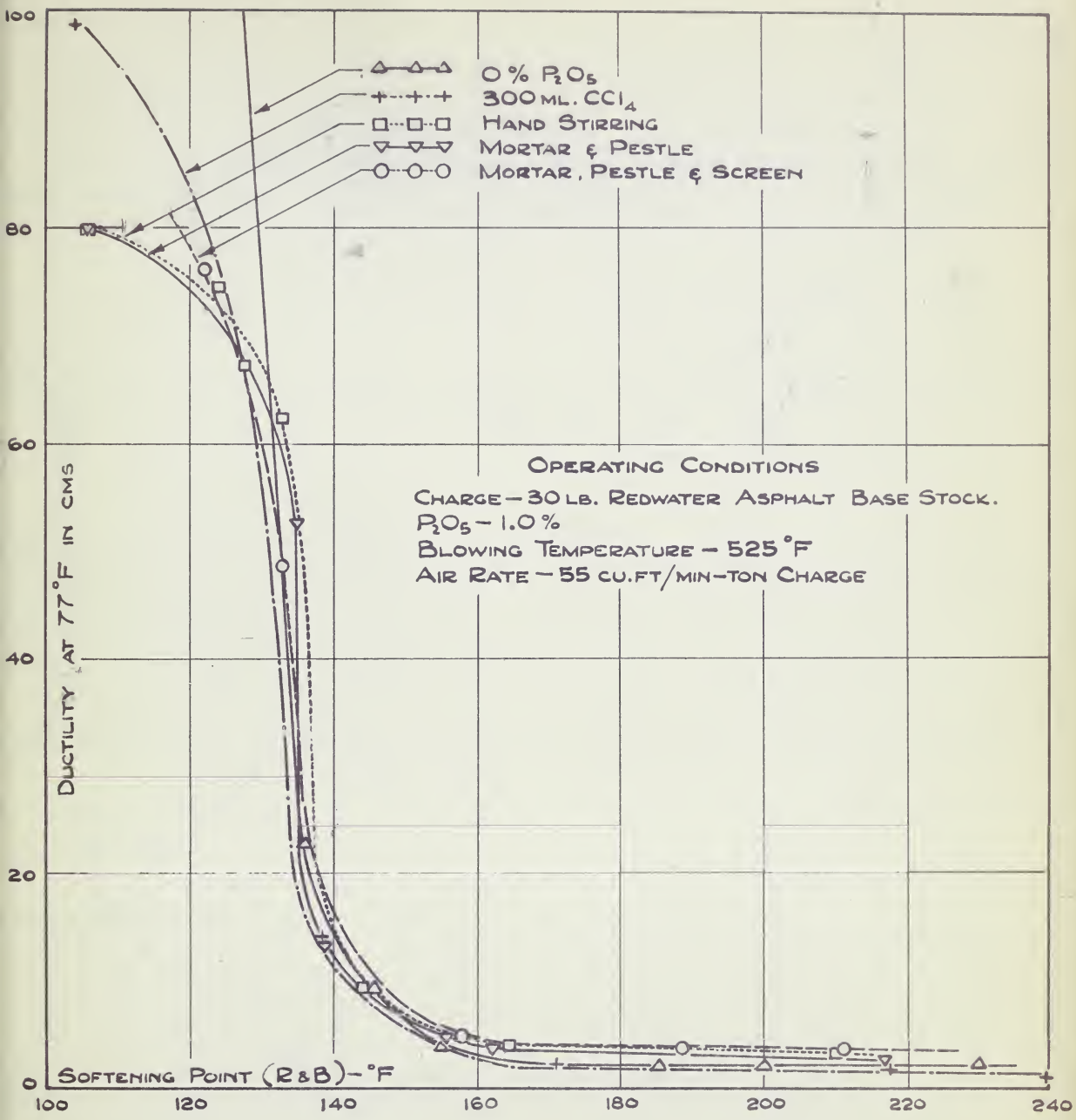

FIG.29. EFFECT OF DISPERSION METHOD FOR PHOSPHORUS PENTOXIDE ON DUCTILITY .

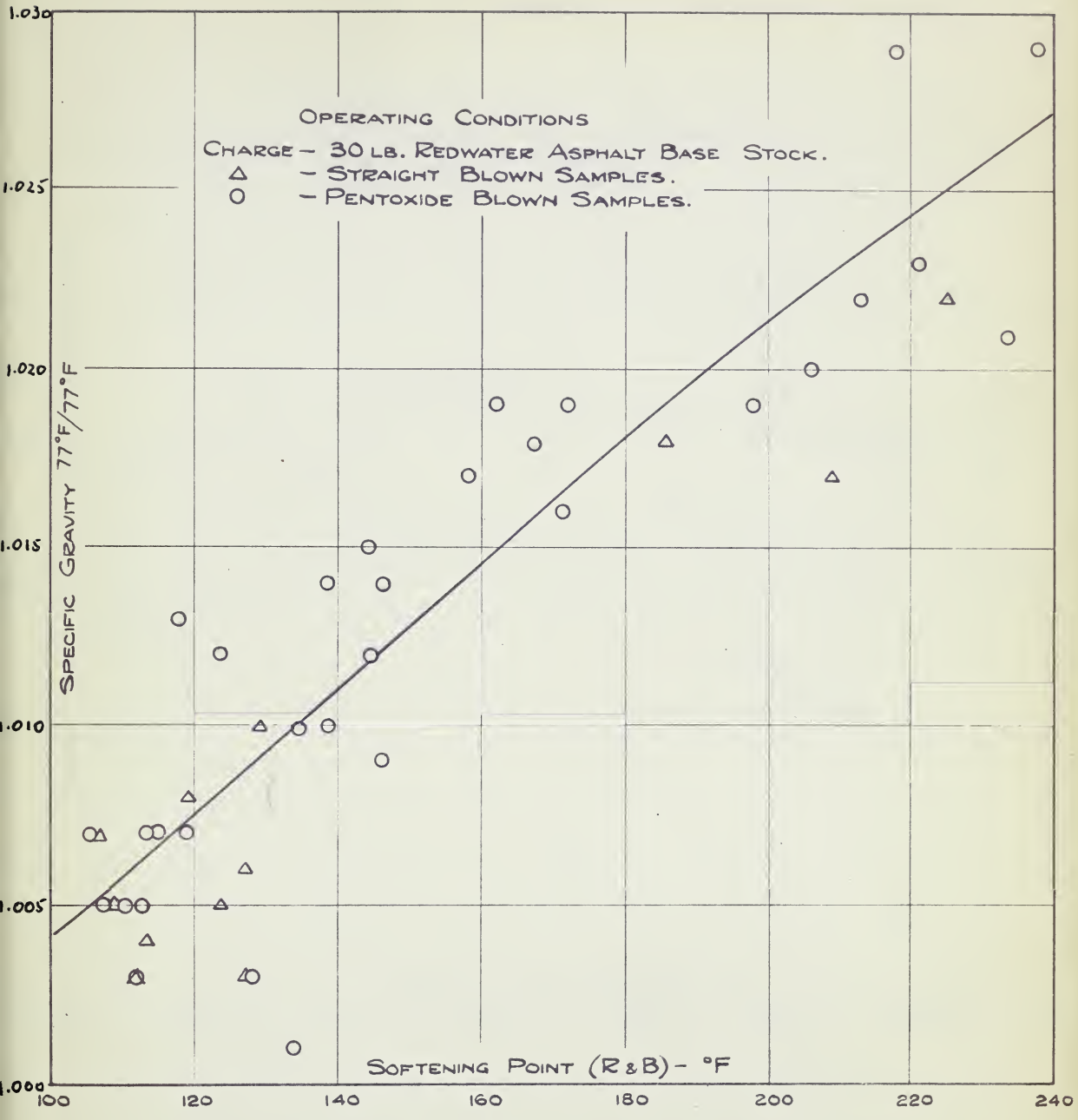

FIG. 30. EFFECT OF AIR BLOWING ON SPECIFIC GRAVITY.

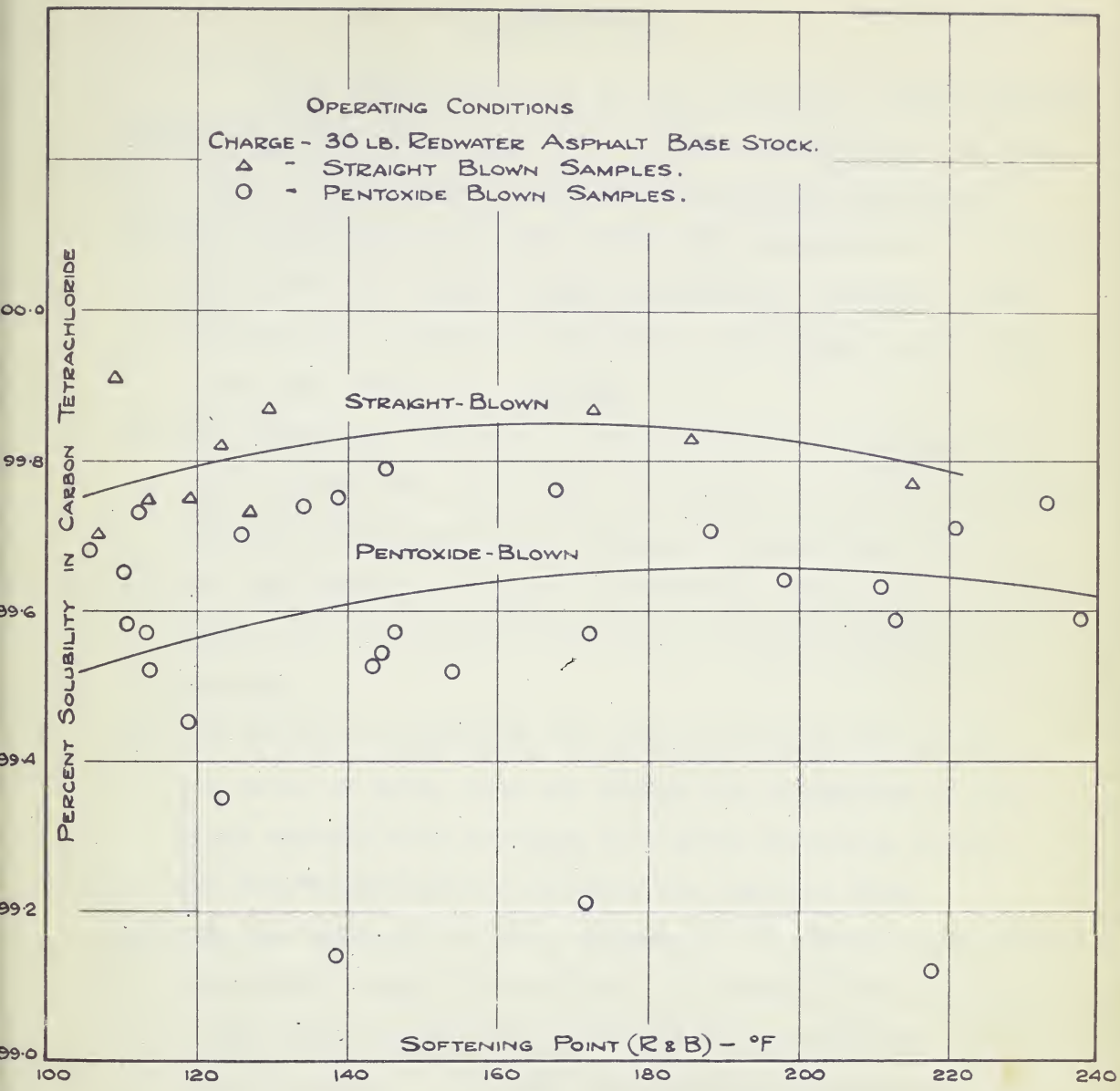

Fig. 31. Effect of Phosphorus Pentoxide on Solubility in Carbon Tetrachloride.

IX. CONCLUSIONS

This investigation of the air blowing of vacuum reduced Redwater asphalt base stock with special reference to the use of phosphorus pentoxide suggests the following conclusions:

(1) The properties of the base stock are changed by air blowing. The product is harder (lower penetration), heavier, lower in ductility, higher in viscosity, and higher in softening point than before the blowing.

(2) The fractional composition of the asphalt is changed with air blowing; the asphaltenes increasing, the resins decreasing and the oily constituents changing comparatively little.

(3) The mean molecular weights of the three fractions (asphaltenes, resins and oily constituents) are increased markedly on air blowing.

(4) The effect of increasing the blowing temperature or the air rate, or both, does not change the properties of the final asphalt with relation to a given softening point, but does significantly decrease the reaction time.

(5) With the addition of small amounts of phosphorus pentoxide, the reaction time, penetration, and Saybolt Furol viscosity of the blown asphalt are increased appreciably for a given softening point. With the same method of dispersing the phosphorus pentoxide, the increase is dependent on the quantity of phosphorus pentoxide, at least in the range from zero to one percent.

(6) With the same dispersing method for the phosphorus pentoxide, asphalts blown to softening point less than 130 °F. with 0.5 and 1.0 percent pentoxide showed a much lower ductility than those blown with 0 and 0.25 percent pentoxide. For higher softening point asphalts, there is no appreciable differences in the ductilities obtained.

(7) The use of the residue formed from a phosphorus pentoxide test produced the same general effect on the reaction time curve, penetration-softening point, Saybolt Furol viscosity-softening point, and ductility-softening point relationships as obtained with the use of fresh phosphorus pentoxide.

(8) The method of dispersing the phosphorus pentoxide in the asphalt base stock is comparable in importance to the amount of phosphorus pentoxide used. With a better method of dispersion, a greater increase in penetration and viscosity and a greater decrease in reaction time, as referred to a given softening point, are obtained. The decrease in reaction time appears almost contradictory to the increase in penetration. The phenomenon is not clearly understood.

APPENDIX I

ANALYSIS OF THE RESIDUE

The standard procedures of the Association of Official Agricultural Chemists (31) were used to determine the percent phosphorus pentoxide in the residue. A summary of the procedures is presented here.

A representative sample of the residue is ashed at low temperature with sodium carbonate and sodium nitrate to volatilize off the carbonaceous material. The purpose of the sodium carbonate and sodium nitrate is to prevent loss of phosphorus pentoxide during ashing, by converting it to sodium phosphate. The ash is dissolved in nitric acid and the phosphate in solution is precipitated as ammonium phosphomolybdate with ammonium molybdate. The precipitate is then dissolved with dilute ammonium hydroxide, and the phosphate reprecipitated as magnesium ammonium phosphate by the addition of magnesia reagent (magnesium chloride and ammonium chloride in ammoniacal solution). A double precipitation was necessary to obtain a precipitate entirely free from interfering substances. The precipitate is weighed and the percent phosphorus pentoxide calculated.

APPENDIX II

TEST METHODS

Softening point (Ring and Ball)	ASTM D36-26
Penetration at 32 °F., 200 grams, 60 seconds	ASTM D243-36
77 °F., 100 grams, 5 seconds	
100 °F., 100 grams, 5 seconds	
115 °F., 50 grams, 5 seconds	
Saybolt Furol viscosity at 210 °F.	ASTM D88-44
250 °F.	
275 °F.	
Ductility at 77 °F.	ASTM D113-44
Specific gravity at 77 °F.	ASTM D70-27
Solubility in carbon tetrachloride	ASTM D165-42
Float test at 122 °F.	ASTM D139-27
Flash point (Cleveland open cup)	ASTM D92-46

APPENDIX III

DETERMINATION OF ASPHALTENES, RESINS AND OILY CONSTITUENTS

The procedure employed for the analyses follows the method proposed by O. G. Strieter (39). A summary of the modified procedure is presented here.

The asphalt is extracted with normal pentane to obtain soluble resins and oily constituents and insoluble asphaltenes. The resins and oily constituents are separated by dispersing them on anhydrous alumina. The unadsorbed oily constituents are recovered by extraction with normal pentane. The resins adsorbed on the alumina are recovered by eluting with benzene and methanol.

The details of the modifications are as follows: Instead of the 35 grams of Fuller's earth as used in Strieter's procedures, 100 grams of anhydrous alumina, technical grade, were used for adsorbing the resins. According to Mack (24), the resins undergo some changes in composition in the Fuller's earth in which a material is recovered which behaves something like asphaltenes. It was found that after the alumina mixture was transferred to the Soxhlet thimble, 2 hours extraction with pentane was sufficient. The adsorbed resins were eluted in a 600 ml beaker with four 50 ml portions of methyl alcohol-benzene solution (10ml of anhydrous methanol to 90 ml of c.p. benzene).

APPENDIX IV

PROCEDURE FOR DETERMINING MOLECULAR WEIGHTS OF ASPHALTENES, RESINS AND OILY CONSTITUENTS

Average molecular weights were obtained by a cryoscopic method using the depression of the freezing point of water-saturated benzene as the criterion.

Freezing points were determined in a glass test tube one inch in diameter. This test tube was inserted in a larger test tube, 1½ inches in diameter, and the whole was immersed in an ice bath. The benzene solution in the inner test tube was agitated by a wire stirrer operated by a small motor. The freezing point depression of benzene solution is seriously affected by changes in moisture content due to changes in the humidity of the air. This source of error was avoided by first saturating the benzene with water. To a liter of benzene 15 ml of distilled water were added. The mixture was heated to 125 °F.; upon cooling, the solution became cloudy. The method of measuring the freezing point was as follows:

About 25 to 30 grams of water-saturated benzene were weighed into the inner test tube, the apparatus assembled, and temperature readings with a Beckmann thermometer were taken at regular intervals. To prevent super-cooling of more than 0.2 °C., the solution was seeded as it passed through the freezing temperature by inserting crystals of benzene into it by means of a fine wire passing through a glass capillary inserted into the inner tube. During cooling, readings were taken at regular

time intervals over a period of about 15 minutes. A typical freezing point curve was obtained which showed rapid initial cooling and supercooling, followed by a rapid rise in temperature when crystallization began, and which showed a nearly constant temperature decrease as crystallization proceeded. To get true freezing point from such a curve, the portion of the curve recording the last rate of cooling was extended back to intersect the initial rapid cooling portion of the curve. The temperature at this point of intersection was taken as the true freezing point of the benzene.

Having determined the freezing point of the solvent accurately, add about 0.3 grams, accurately weighed, of the asphalt fraction into the water-saturated benzene and determine the freezing point of the solution in the same manner as above. Record the freezing point depression, substitute in the equation below and calculate molecular weight.

$$M = \frac{(F - \Delta T)\ W}{\Delta T\ S\ B}$$

where M = unknown molecular weight

F = cryoscopic constant of benzene as determined using naphthalene = 65

W = weight of solute in grams

ΔT = freezing point depression, $^{o}C.$

B = constant depending upon water content of solution; is equal to 1.005 for water-saturated benzene and 1.000 for dry benzene

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